PB-249 911

ANNUAL CATALYST RESEARCH PROGRAM REPORT. APPENDICES. VOLUME III

Health Effects Research Laboratory
Research Triangle Park, North Carolina

September 1975

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

EPA-[illegible]
September 1975

023055

064041

PB 249 911

Ecological Research Series

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ECOLOGICAL RESEARCH series. This series describes research on the effects of pollution on humans, plant and animal species, and materials. Problems are assessed for their long- and short-term influences. Investigations include formation, transport, and pathway studies to determine the fate of pollutants and their effects. This work provides the technical basis for setting standards to minimize undesirable changes in living organisms in the aquatic, terrestrial and atmospheric environments.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

1. REPORT NO. EPA-600/3-75-010d	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE ANNUAL CATALYST RESEARCH PROGRAM REPORT Appendices, Volume III		5. REPORT DATE September 1975 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Criteria and Special Studies Office		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Health Effects Research Laboratory Office of Research & Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711		10. PROGRAM ELEMENT NO. 1AA002 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Same as above		13. TYPE OF REPORT AND PERIOD COVERED Annual Program Status 1/74-9/74 14. SPONSORING AGENCY CODE EPA-ORD

15. SUPPLEMENTARY NOTES

This is the Summary Report of a set (9 volumes plus Summary).
See EPA-600/3-75-010a thru 010c, 010e thru 010j.Report to Congress.

16. ABSTRACT

This report constitutes the first Annual Report of the ORD Catalyst Research Program required by the Administrator as noted in his testimony before the Senate PUblic Works Committee on November 6, 1973. It includes all research aspects of this broad multi-disciplinary program including: emissions characterization, measurement method development, monitoring, fuels analysis, toxicology, biology, epidemiology, human studies, and unregulated emissions control options. Principal focus is upon catalyst-generated sulfuric acid and noble metal particulate emissions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Catalytic converters Sulfuric acid Desulfurization Catalysts Sulfates Sulfur Health	Automotive emissions Unregulated automotive emissions Health effects (public)	

18. DISTRIBUTION STATEMENT Available to public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 242
	20. SECURITY CLASS (This page) Unclassified	

EPA-600/3-75-010d
September 1975

ANNUAL CATALYST RESEARCH PROGRAM REPORT APPENDICES

Volume III

by

Criteria and Special Studies Office
Health Effects Research Laboratory
Research Triangle Park, North Carolina 27711

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
HEALTH EFFECTS RESEARCH LABORATORY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

CONTENTS

Page

CATALYST RESEARCH PROGRAM ANNUAL REPORT

EXECUTIVE SUMMARY 1
INTRODUCTION 5
PROGRAM SUMMARY 7
TECHNICAL CONCLUSIONS 17
DISCUSSION 22
REFERENCES 45

APPENDICES TO CATALYST RESEARCH PROGRAM ANNUAL REPORT

VOLUME 1

A. OFFICE OF AIR AND WASTE MANAGEMENT

A1. AUTOMOTIVE SULFATE EMISSIONS 1
A2. GASOLINE DE-SULFURIZATION - SUMMARY 53
  A2.1 Control of Automotive Sulfate Emissions through Fuel Modifications 55
  A2.2 Production of Low-sulfur Gasoline 90

VOLUME 2

B. OFFICE OF RESEARCH AND DEVELOPMENT

B1. FUEL SURVEILLANCE

  B1.1 Fuel Surveillance and Analysis 1
  B1.2 The EPA National Fuels Surveillance Network. I. Trace Constituents in Gasoline and Commercial Gasoline Fuel Additives . . 19

B2. EMISSIONS CHARACTERIZATION

  B2.1 Emissions Characterization Summary 44
  B2.2 Sulfate Emissions from Catalyst- and Non-catalyst-equipped Automobiles 45
  B2.3 Status Report: Characterize Particulate Emissions - Prototype Catalyst Cars 68
  B2.4 Status Report: Characterize Particulate Emissions from Production Catalyst Cars . . 132
  B2.5 Status Report: Survey Gaseous and Particulate Emissions - California 1975 Model Year Vehicles 133
  B2.6 Status Report: Characterization and Measurement of Regulated, Sulfate, and Particulate Emissions from In-use Catalyst Vehicles - 1975 National Standard 134
  B2.7 Gaseous Emissions Associated with Gasoline Additives - Reciprocating Engines. Progress Reports and Draft Final Report - "Effect of Gasoline Additives on Gaseous Emissions" . 135

Page

B2.8 Characterization of Gaseous Emissions from Rotary Engines using Additive Fuel - Progress Reports 220
B2.9 Status Report: Exploratory Investigation of the Toxic and Carcinogenic Partial Combustion Products from Oxygen- and Sulfur-containing Additives 232
B2.10 Status Report: Exploratory Investigation of the Toxic and Carcinogenic Partial Combustion Products from Various Nitrogen-containing Additives 233
B2.11 Status Report: Characterize Diesel Gaseous and Particulate Emissions with Paper "Light-duty Diesel Exhaust Emissions" 234
B2.12 Status Report: Characterize Rotary Emissions as a Function of Lubricant Composition and Fuel/Lubricant Interaction 242
B2.13 Status Report: Characterize Particulate Emissions - Alternate Power Systems (Rotary) 243

VOLUME 3

B.3 Emissions Measurement Methodology

B3.1 Emissions Measurement Methodology Summary 1
B3.2 Status Report: Develop Methods for Total Sulfur, Sulfate, and other Sulfur Compounds in Particulate Emissions from Mobile Sources 2
B3.3 Status Report: Adapt Methods for SO_2 and SO_3 to Mobile Source Emissions Measurements 3
B3.4 Evaluation of the Adaption to Mobile Source SO_2 and Sulfate Emission Measurements of Stationary Source Manual Methods. 4
B3.5 Sulfate Method Comparison Study. CRC APRAC Project CAPI-8-74 17
B3.6 Determination of Soluble Sulfates in CVS Diluted Exhausts: An Automated Method 19
B3.7 Engine Room Dilution Tube Flow Characteristics 41
B3.8 An EPA Automobile Emissions Laboratory 52
B3.9 Status Report: Protocol to Characterize Gaseous Emissions as a Function of Fuel and Additive Composition - Prototype Vehicles 89
B3.10 Status Report: Protocol to Characterize Particulate Emissions as a Function of Fuel and Additive Composition 90
B3.11 Interim Report and Subsequent Progress Reports: Development of a Methodology for Determination of the Effects of Diesel Fuel and Fuel Additives on Particulate Emissions 192

Page

B3.12 Monthly Progress Report #7: Protocol to Characterize Gaseous Emissions as a Function of Fuel and Additive Composition 200
B3.13 Status Report: Validate Engine Dynomometer Test Protocol for Control System Performance 218
B3.14 Fuel Additive Protocol Development 221
B3.15 Proposed EPA Protocol: Control System Performance 231

VOLUME 4

B3.16 The Effect of Fuels and Fuel Additives on Mobile Source Exhaust Particulate Emissions 1

VOLUME 5

B3.17 Development of Methodology to Determine the Effect of Fuels and Fuel Additives on the Performance of Emission Control Devices 1
B3.18 Status of Mobile Source and Quality Assurance Programs 260

VOLUME 6

B4. Toxicology

B4.1 Toxicology: Overview and Summary 1
B4.2 Sulfuric Acid Effect on Deposition of Radioactive Aerosol in the Respiratory Tract of Guinea Pigs, October 1974 38
B4.3 Sulfuric Acid Aerosol Effects on Clearance of Streptococci from the Respiratory Tract of Mice. July 1974 63
B4.4 Ammonium and Sulfate Ion Release of Histamine from Lung Fragments 89
B4.5 Toxicity of Palladium, Platinum and their Compounds 105
B4.6 Method Development and Subsequent Survey Analysis of Experimental Rat Tissue for PT, Mn, and Pb Content, March 1974 128
B4.7 Assessment of Fuel Additives Emissions Toxicity via Selected Assays of Nucleic Acid and Protein Synthesis 157
B4.8 Determination of No-effect Levels of Pt-group Base Metal Compounds Using Mouse Infectivity Model, August 1974 and November 1974 (2 quarterly reports) 220
B4.9 Status Report: "Exposure of Tissue Culture Systems to Air Pollutants under Conditions Simulating Physiologic States of Lung and Conjunctiva" 239

✓

Page

B4.10 A Comparative Study of the Effect of Inhalation of Platinum, Lead, and Other Base Metal Compounds Utilizing the Pulmonary Macrophage as an Indicator of Toxicity 256
B4.11 Status Report: "Compare Pulmonary Carcinogenesis of Platinum Group Metal Compounds and Lead Compounds in Association with Polynuclear Aromatics Using *in vivo* Hamster System 258
B4.12 Status Report: Methylation Chemistry of Platinum, Palladium, Lead, and Manganese 263

VOLUME 7

B.5 Inhalation Toxicology
B5.1 Studies on Catalytic Components and Exhaust Emissions 1

B.6 Meteorological Modelling
B6.1 Meteorological Modelling - Summary 149
B6.2 HIWAY: A Highway Air Pollution Model 151
B6.3 Line Source Modelling 209

B.7 Atmospheric Chemistry
B7.1 Status Report: A Development of Methodology to Determine the Effects of Fuel and Additives on Atmospheric Visibility 233
Monthly Progress Report: October 1974 255
B7.2 Status Report: Develop Laboratory Method for Collection and Analysis of Sulfuric Acid and Sulfates 259
B7.3 Status Report: Develop Portable Device for Collection of Sulfate and Sulfuric Acid 260
B7.4 Status Report: Personal Exposure Meters for Suspended Sulfates 261
B7.5 Status Report: Smog Chamber Study of SO_2 Photo-oxidation to SO_4 under Roadway Condition 262
B7.6 Status Report: Study of Scavenging of SO_2 and Sulfates by Surfaces near Roadways 263
B7.7 Status Report: Characterization of Roadside Aerosols: St. Louis Roadway Sulfate Study 264
B7.8 Status Report: Characterization of Roadside Aerosols: Los Angeles Roadway Sulfate Study 269

Page

VOLUME 8

B.8 Monitoring

B8.1 Los Angeles Catalyst Study. Background Preliminary Report 1
B8.2 Los Angeles Catalyst Study; Summary of Background Period (June, July, August 1974) 13
B8.3 Los Angeles Catalyst Study Operations Manual (June 1974, amended August 1974) 33
B8.4 Collection and Analysis of Airborne Suspended Particulate Matter Respirable to Humans for Sulfates and Polycyclic Organics (October 8, 1974). . .194

VOLUME 9

B.9 Human Studies

B9.1 Update of Health Effects of Sulfates, August 28, 1974 . 1
B9.2 Development of Analytic Techniques to Measure Human Exposure to Fuel Additives, March 1974 7
B9.3 Design of Procedures for Monitoring Platinum and Palladium, April 1974. 166
B9.4 Trace Metals in Occupational and Non-occupationally Exposed Individuals, April 1974 178
B9.5 Evaluation of Analytic Methods for Platinum and Palladium. 199
B9.6 Literature Search on the Use of Platinum and Palladium. 209
B9.7 Work Plan for Obtaining Baseline Levels of Pt and Pd in Human Tissue 254

Appendix B3.1

Emissions Measurement Methodology Summary

The major effort in the ORD Fuel and Fuel Additive, Catalyst, and Mobile Source Emissions Research Programs has involved detailed characterization of non-regulated gaseous and particulate pollutants from mobile sources. The effect of fuel composition, fuel additives, and control devices have been the predominant determinants of interest. Appendix B2 covered details of the emissions characterization repeats of the program. Within this appendix, those programs specifically directed toward development of standardized measurement methods to be routinely used for the assessment of particulate, sulfate and SO_2 emissions from non-catalyst and catalyst equipped vehicles will be reviewed.

Appendix B3.2

Status Report

ROAP 21BCE

Task 043

Develop Methods for Total Sulfur, Sulfate, and Other Sulfur Compounds in Particulate Emissions from Mobile Sources

This in-house project is designed to provide the methodology necessary to analyze the particulate matter collected from mobile source emissions. The fate of organic sulfur compounds both present in fuel and added in additive packages has not been fully defined. While a sulfate method has been developed, other methods are needed for total sulfur and other inorganic and organic sulfur compounds. X-ray fluorescence methods are being investigated to measure total sulfur. Instrumental methods to permit the analysis of sulfuric acid in addition to the method previously developed may be evaluated. Other inorganic sulfides, sulfites, as well as organic sulfur compounds, will be investigated on the basis of probable impact.

Status:

Recruitment is under way and the project should be implemented in the second quarter of FY75.

Appendix B3.3

Status Report

ROAP 21BCE

Task 042

Adapt Methods for SO_2 and SO_3 to Mobile Source Emissions Measurements

This in-house project will further implement and provide more definitive efforts to develop methodology applicable to use in mobile source analyses. Orginally, efforts have provided exploratory methodology to determine sulfur dioxide concentrations in mobile source emissions. This effort will be expanded to provide better methods and to correlate these with other methodology. The need is for real time monitors for gaseous sulfur emissions which may be used to monitor systems in operation.

Status:

Employment of appropriate manpower is under way and should be completed shortly allowing activation of this project.

Appendix B3.4

EVALUATION OF THE ADAPTATION TO MOBILE SOURCE SO_2 AND SULFATE EMISSIONS MEASUREMENT OF STATIONARY SOURCE MANUAL METHODS

R.L. Bradow

In recent months a variety of qualification experiments on the validity of isopropanol-water trapping of SO_3 with mobile source emissions have been reported with widely varient results.[1,2] A group at Chrysler Corporation has reported essentially unqualified success with EPA method 8[3] in this application.[1] Ethyl Corporation workers report erraneous of high sulfate values with doped SO_2 both with and without auto exhaust added.[2] General Motors has suggested that use of technical grade isopropyl alcohol at least partially avoids the problem of SO_2 trappings in the sulfate bubbler.[4] Ford raises a number of issues regarding the validity of the method on a theoretical basis[5] relying mainly on supporting data furnished by Walden Corporation in stationary source qualification experiments.[6] It is the purpose of this study to examine the procedures used by the differing research groups in detail and to offer explanations of the variable results obtained.

In the Chrysler work experiments with single cylinder ASTM grade isooctane , engines operated on an essentially sulfur-free fuel, were performed in order to establish the basic validity of IPA-H_2O trapping of sulfates! No apparent sulfate was found with the base isooctane indicating that positive interferences were not present with that exhaust. SO_2 tank gas in the exhaust pipe, in the sampling in impingers or in a bag added to the iso-octane exhaust also did not give any apparent sulfate. Lab bench studies with tank SO_2 confirmed no SO_2 trapping or oxidation. Exhaust from 0.1% sulfur gasoline did produce apparent sulfate and this was confirmed by gravimetric determination of the barium precipitate. The results of the gravimetric method were 75% of those obtained by titration to a thorin end point. Interferences from exhaust system particles and incomplete SO_4 trapping were also checked experimentally and ruled out.

Ethyl corporation also operated a single cylinder engine on isooctane with tank SO_2 added to the exhaust and found that 10-14% of the SO_2 was retained in the first bubbler and erroneously measured as sulfate. [2] Bench experiments also indicated retention of SO_2 measured as sulfate in the first bubbler. This could be partially eliminated by pre-acidifying the bubblers, with sulfuric acid. However, since the added sulfuric acid constitutes a high blank, the detection of trace quantities of sulfate involves determination of a small difference between two large quantities. Ethyl workers also reported great variability in engine test results rendering the method almost unusable.

The Ethyl and Chrysler experiments, therefore, are apparently in direct conflict. Since the G. M. experiments indicated differing results with different grades of isopropanol, it is probable that details of the methodology may account for the observed variations in qualification test results. Therefore, the methods employed by Ethyl and Chrysler were examined more closely.

Chrysler Corporation workers used a flowmeter followed by series of 4 midget impingers containing 15 ml. of 80% isopropyl alcohol (IPA) - water solution backed by a DuPont model 411 UV photometric SO_2 analyzer. Sample was pulled through the train at a flow rate of 5 liters/min. for 20 to 30 minutes to obtain a sample of 85 to 120 liters of gas. After sampling the contents,of all four bubblers was rinsed into a 100cc volunetrics flask with 80% IPA and a 25cc. aliquot was immediately titrated with 0.01 N $BaCl_2$ solution to a thorin-endpoint. A stainless steel exhaust proble was used to obtain the sample. Repeatable results were found in a wide variety of experiments.

The Ethyl Corporation group used a standard EPA sampling train using 100 ml. of 80% IPA in the first Greenberg-Smith impinger, this solution plus 2% peroxide in the second and third impingers and a fourth dry impinger followed by flow monitoring appartus. Flowrates of 1.5 to 2.5 liters/minute for periods of 1 hour. In many of the experiments an initial quantity of sulfuric acid of 5 to 10 ml. was added to the first bubbler to suppress SO_2 solubility which otherwise obscurred the results. Such a practice has been recommended elsewhere.[7,8]

After volunetric transfer an aliquot of each of the impinger contents was titrated with 0.0/N $BaClO_4$ to a thorin end-point. Standing time for the impinger samples was not controlled and varied from 24 to 48 hours. The solutions were also evaporated to increase the sulfate concentrations and, thus, the sensitivity of the method. Cle Clearly, both groups have drastically modified the Federal Register method in both details of glass ware, sampling and analytical determination. In order to resolve the source of the apparent differences an experimental program was instituted to investigate the influence of some of the variances on the analytical results.

The experiments performed had as there goals:

1. Establishment of test repeatability with engine exhaust.
2. Investigation of possible interference in sulfate determinations from trapped SO_2.
3. Establishment of the influence of analysis variations, glass ware type, flow rates and trapping solution variation on test results.

EXPERIMENTAL:

Method 8 sampling trains were attached to the exhaust pipe of a 350 CID 1972 Chevrolet engine equipped with an automatic transmission and operated on an engine dynanometer test stand. The engine was operated at 30 mph and 32.0 ft-lbs of torque, corresponding to somewhat greater than road load. Fuels used were the EPA reference fuel with 125 ppm sulfur, that fuel doped to 0.100 wt. % sulfur with thiophene, and ASTM grade isooctane containing less than 1 ppm sulfur. The sampling trains were attached by means of Swagelok fittings and a metal ball joint to a ¼ " stainless steel tube welded into the exhaust pipe. Inside the exhaust pipe the tube made a 90° bend and a 2 " straight section was faced upstream and centered in the pipe. Figure 1 indicates the location of the bubbler trains.

Bubbler trains were assembled and operated in a manner as nearly identical as possible with the trains used by Chrysler[1] and Ethyl[2]. In addition, a third micro method 8 train, using ball-joint equipped midget impingers was set up in a manner recommended by the stationary source group. This train included a single IPA-water bubbler, one H_2O_2 bubbler, and a dry bubbler.

Methods of analysis included $BaClO_4$ titration to a mixed thorin-methylene blue end point for the EPA modified train as per the Federal Register[3]. For the Chrysler and Ethyl modifications workup and analysis procedures those reported in the literature for those methods were used[1,2].

In several experiments with isooctane as a fuel a 500 ppm SO_2 in N_2 tank gas was injected upstream of the bubbler trains through a second upstream-facing probe welded in the exhaust pipe. Injection rates were controlled to give a final exhaust concentration of 10.0 ppm SO_2. The point of SO_2 injection is also shown in Figure 1.

RESULTS AND DISCUSSION:

Table 1 summarizes the results obtained with the EPA method using 127 and 1000 ppm wt./wt. sulfur in the EPA reference fuel and the non-catalyst engine test stand. The overall recovery of SO_2 was good, averaging 97.5 % of the charge. The repeatability of the method was also good, with a standard deviation of 1.7 % for 6 runs.

In all the runs there was apparent sulfate ranging from 9 to 37 % of the total SO_2. In experiments with added SO_2, apparent sulfate was again detected at about 25 % of the charged SO_2. In the last three runs an attempt was made to purge trapped SO_2 from the first bubbler by drawing through room air at the sample rate for 10 minutes. Wolden researchers had previously established that this procedure is helpful in avoiding artifact sulfate analysis[6] with stack samples. However, in these experiments, purge air had no significant effect in reducing apparent sulfate. Thus, it appears that this procedure is capable of reproducible results but produces a sulfate artifact of 15-25 % of the charged SO_2.

Samples of the first bubbler contents from runs 13 and 14 were diluted 20:1 with distilled water and analyzed by the West-Gaeke method for sulfite. The purpose of these experiments was to determine whether the trapped material in those bubblers would be dissolved SO_2. Insignificant amounts of SO_2 were found. Samples of the barium precipitate were centrifuged out and collected for X-ray diffraction analysis. The X-ray diffraction pattern shows conclusively that the material is barium sulfate, not sulfite. Therefore, it appears that SO_2 analyzed by this method is subject to oxidation of part of the

SO_2 to SO_4 in the sampling process.

Table 2 presents results from the Chrysler procedure. Again, highly reproducible results were obtained and mean and standard deviation for sulfur recovery were 92.5% and 2.9% respectively. Apparent sulfate was again found, this time at the 14% level.

In this method four bubblers in series were used at rather high flow rates for the small size of the train. Apparent sulfate in only slightly decreasing amounts was found in each of the sulfate bubblers prior to the hydrogen peroxide SO_2 trap. Expressed as a percentage of the apparent sulfate collected, bubbler 1 contained 31.0%, bubbler 2 24.6%, bubbler 3 22.5%, and bubbler 4 21.6% for the average of four runs. In the Chrysler experiments the contents of all four bubblers were combined prior to titration and no information on the relative collection efficiency of the two bubblers for real sulfate aerosols was presented[1]. On the basis of these tests, either the bubbler train collects artifact sulfate or it is highly inefficient. However, Ethyl data suggests that the first bubbler is fairly efficient for collection of synthetic sulfate mists[2]. In those experiments a collection efficiency of about 80% was obtained. It, therefore, appears that artifact sulfate is being formed in each IPA bubbler in the train. It is interesting to note that the first two bubblers do contain somewhat more sulfate than the last two. If the content of the last two bubblers is taken to be the artifact sulfate content of the first two, an approximate value for the real sulfate can be obtained by difference. Thus, the real sulfate would be about 10% of the apparent method 8 sulfate or about 2% of the SO_2. This value is in good agreement with sulfate values found in non-catalyst cars by air filtration methods.[4]

Table 2 also presents attempts to reproduce a Chrysler qualification experiment in which SO_2 was added to an auto exhaust from isooctane which contained no sulfur. According to Chrysler reports, no apparent sulfate was found. However, in the present study, apparent sulfate was found in approximately the same proportion as that obtained from the sulfur-bearing fuel. Clearly this indicates artifact formation occurs with the Chrysler procedure.

Table 3 presents data obtained with the Ethyl method. Data scatter was poor as Ethyl had previously found.[2] Again, apparent sulfate was found in all experiments including those with isooctane.

In all three procedures, blank experiments were run with the collecting solutions and with isooctane exhaust to insure that interferences or contaminants were not biasing results.

CONCLUSION:

Method 8 variants clearly produce apparent sulfate when used in auto exhaust applications. It appears that this occurs by oxidation of the SO_2 to sulfate, probably in the collection solution. Further experiments are in progress to elucidate this point and to compare Method 8, Goksoyr-Ross, and filtration procedures with catalyst-equipped engines.

It appears that previous Method 8 work on non-catalyst engines must be seriously in error.

Table 1

EPA Method

Run No.	Fuel S wt. %	Sample Flow Rate ℓ/min	Time min.	Total Moles	μ Moles $SO_4^=$	μ Moles SO_2	% Conv.	Ppm SO_2 in exhaust	Calc.	% Recov.
10	0.100	1.65	20	1.326	6.773	68.78	8.9	56.96	58.50	97.4
11	0.100	1.65	20	1.326	—	73.46	—	55.40	58.50	94.7
12	0.0127	1.42	40	2.282	4.539	11.801	27.6	7.160	7.429	96.4
13*	0.0127	1.16	60	2.79	7.761	13.058	37.2	7.458	7.429	100.4
14*	0.0127	2.40	60	5.787	6.424	35.752	15.2	7.287	7.429	98.1
15*	0.0127	2.40	60	5.787	6.424	35.612	15.3	7.263	7.429	97.8
										$\bar{x}$ = 97.5
										σ 1.7
10 ppm SO_2 injected - isooctane fuel										
1	<1	2.40	30	2.89	5.84	22.9	20.2	9.93	10	99
2	<1	2.40	30	2.89	9.07	20.4	30.7	10.2	10	102

* Air drawn through bubbler for 10 minutes.

Table 2

Chrysler Method

A: EPA Reference Fuel - 1000 ppm S

Run No.	Sample Vol.	Sample Moles	μMoles $SO_4^=$	μMoles SO_2	% Convr.	Meas. ppm SO_2	Calc. ppm SO_2	% Recov.
1	144	5.787	44.68	259.39	14.7	52.5	58.5	89.8
2	144	"	41.39	266.74	13.7	53.2	58.5	91.0
3	144	"	42.25	268.69	13.6	53.13	58.5	91.8
4	144	"						
			41.49	288.41	12.6	56.99	58.5	97.4
		$\bar{x}$	42.43	270.81	13.6	54.1		92.5
		σ	1.34	10.74	0.74	1.7		2.9

B. Isooctane + 10 ppm SO_2
< 1 ppm S

Run No.	Sample Vol.	Sample Moles	μMoles $SO_4^=$	μMoles SO_2	% Convr.	Meas. ppm SO_2	Calc. ppm SO_2	% Recov.
5	72	2.894	14.89	11.22	57.03	9.02	10.0	90.2
6	72	2.894	12.04	13.41	47.3	8.79	10.0	87.9

Table 3

Ethyl Method

Sampling conditions: 3 lpm - 1 hour - 7.234 moles of sample gas

Run No.	Fuel S ppm	μ Moles $SO_4^=$	μ Moles SO_2	% Conver.	Meas. ppm SO_2	Calc. ppm SO_2	% Recovered
1	127	23.4	49.4	32.14	10.05	7.429	135
2	127	5.51	44.6	10.9	6.93	7.429	93
5	127	3.36	67.9	5.5	8.86	7.429	119
					$\bar{X}$ = 8.62 σ = 1.29		
3	1000	81.8	261.8	23.8	47.8	58.5	82
4	1000	28.65	457	5.9	67.1	58.5	115
6	1000	50.1	437	10.3	72.5	58.5	124
					$\bar{X}$ = 62.5 σ = 10.6		

Isooctane runs - 10 ppm SO_2 injected

7	<1	8.7	45.9	18.9	7.65	10.0	76
8	<1	9.3	50.5	15.6	8.27	10.0	83

1. Chrysler Corporation, Response to a request for information on sulfate emissions in the Federal Register, 39, No. 47, dated May 6, 1974.

2. Ethyl Corporation, Response to a request for information on sulfates emissions in the Federal Register, 39, No. 47, Dated May 3, 1974.

3. A. Federal Register, 37, No. 221, Part II, 87,075-24 and Appendix I, Nov. 15, 1972.
   B. Seidman, B.I., Anal., Chem., 30, 1680(1968)

4. General Motors Corporation, Response to a request for information on sulfates emissions in the Federal Register, 39, No. 41, dated May 7, 1974.

5. Ford Motor company, Response to a request for information on sulfates emissions in the Federal Register, 39, No. 47, dated May 6, 1974.

6. Driscoll, J., et. al., EPA Report No. EPA-R2-72-105, November, 1972.

7. Fielder, R.S., and Morgan, C.H., Analyt. Chinica Acta, 23, 538 (1960).

8. Schmidt, M., Report on Word Health Organization Project # U.S.3100, July, 1970.

9. Goksyr, H., and Ross, K., J. Inst. Fuel, 35, 177(1972).

10. Lisle, E.S., and Sensenbaugh, J.D., Combustion, 36, 12 (1965).

Appendix B3.5

SULFATE METHOD COMPARISON STUDY

CRC APRAC PROJECT CAPI-8-74

R. L. Bradow

A number of researchers active in the catalyst sulfates field are participating in a study of methods of analysis of sulfate in filter samples. ETCS has prepared 128 filter samples in groups of four, using a 1975 Ford catalyst prototype and a 1972 Chevrolet which has been continuously operated on lead-free fuel. The Ford was operated on low sulfur, 500 pms, and 2000 pms gasolines to obtain three levels of sulfate. Low sulfate samples were obtained, using the Chevrolet on the low sulfur fuel only. Eight Highway Fuel Economy tests were run with each condition giving a total of 32 test runs. Filters were then circulated in groups of twelve to each of 8 participating laboratories for analysis. 32 samples were analyzed by EPA by the barium chloranilate method, and 10 of these were also analyzed by X-ray fluorescence spectroscopy. Other labs use thorin titration, barium sulfate gravimetry, H_2S-methylene blue methods, and a sulfarazo III indicator method.

About half the data is now in, and the balance is expected within the week. Some time will be required for statistical analysis, but barium titration methods seem to give slightly lower results than chloranilate and the H_2S-methylene blue method slightly higher results. X-ray fluorescence proceeds correlate well with sample sulfate loading up to about 400 μg and then seem to roll off somewhat. At loadings of 1500 μg X-ray methods appear to give about 30% low results based on a linear standardization.

It is expected that this project will have an additional role to play in comparison of SO_2 methods and other methods of test for catalyst-related emissions.

Appendix B3.6

Determination of Soluble Sulfates in CVS Diluted Exhausts: An Automated Method

The initial report that catalytic converters originally designed to reduce hydrocarbon, carbon monoxide, and oxides of nitrogen emissions from late model automobiles also promote conversion of SO_2 to SO_3 or H_2SO_4 mist prompted a crash program to find or develop a fast and sensitive methodology for sulfates applicable to car exhausts. Although a number of analytical procedures for sulfates are described in the literature, only a few of these have the sensitivity sufficient to detect soluble sulfates in auto exhaust samples conveniently collectible within the time frame of the Federal Test Procedure.

The automated method described in this report is addressed primarily to the determination of water-soluble sulfates in CVS diluted exhausts from cars run on nonleaded fuels. The method is quite general, however, and may be used for trace analysis of sample sulfates which can be leached out with water or aqueous alcoholic solutions.

The method, first developed elsewhere (1), is based on the reaction of sulfate ions with the solid barium salt of chloranilic acid (2,5 dichloro-3,6-dihydroxy-p-benzoquinone). The reaction precipitates out $BaSO_4$ and releases highly uv absorbing acid chloranilate ions, the absorbance of which can be measured with a suitable spectrophotometer and related to sulfate concentration. The sensitivity of the method is greatly enhanced by conducting the reaction in a medium less polar than water, such as ethanol-water or isopropanol-water mixtures, where the solubilities of both $BaSO_4$ and barium chloranilate are reduced. The barium chloranilate method is estimated to have a limiting sensitivity for $SO_4^{=}$ to concentration levels of 0.06 μg/ml (2).

Cations are known to interfere negatively by reacting with the acid chloranilate to form insoluble salts. This interference is easily removed by passing the sample through a column of cation exchange resin in the hydrogen form. Anions such as Cl^-, Br^-, F^-, and PO_4^{---} interfere by precipitating out as barium salts with subsequent release of acid chloranilate ions. Some buffer systems are reported to minimize these anion interferences (3,5). For exhaust samples from cars run on nonleaded fuel, ionic interference was observed to be negligible when filtration on Teflon filters was used as a sample collection technique.

Sampling and Sample Preparation

Sampling methodology involved dilution of the auto exhaust with air in a dilution tunnel. At the temperature the tunnel is operated, SO_3 reacts readily with the available moisture in the exhaust to form H_2SO_4 mist. The acid aerosols are sampled through isokinetic probes and collected on 47 mm diameter 1 μ pore size Fluoropore* filters at flow rates of 28.3 liters per minute. The filters are extracted with 10 ml of 60/40 isopropanol/H_2O solution (60% IPA) in capped polyethylene bottles. Extraction is accomplished by shaking the filters in the capped bottles for at least one minute using a vortex test tube mixer followed by a 10-15 minute soak. The supernatant extract can be analyzed directly in the automated sulfate instrument without further treatment.

---

*Registerd trade mark. Obtainable from Millipore Corporation.

The Automated Sulfate Instrument

A schematic of the principal components of the automated set-up is shown in Figure 1. Hardware requirements include:

a. Reservoir (LR) for the solvent mobile phase (60% IPA).

b. High pressure liquid pump (LP) capable of delivering liquids at flow rates of up to 3 ml/min at pressures as high as 1000 psi. Most liquid pumps used in high pressure liquid chromatography would be satisfactory.

c. Flow or pressure controller (FC).

d. Six-port high pressure switching valve (SV) equipped with interchangeable external loop (L).

e. Ultraviolet detector (D) equipped with appropriate filters or monochromator to isolate a narrow band of radiation centered at 310 nm.

f. Recorder to monitor detector response.

g. Automatic sampler (AS), such as the one used in a Technicon AutoAnalyzer set-up.

h. Peristaltic pump (PP), such as a Technicon proportioning pump, to draw sample into the sampling loop.

i. Cation exchange resin column (CX) - standard 1/4" O.D. x 10" gas chromatographic stainless steel column packed with analytical grade Dowex 50W-X2 (100-200 mesh) cation exchange resin in the hydrogen form.

j. Barium chloranilate column (BC) - standard 1/4" O.D. x 5" gas chromotographic stainless steel column packed with barium chloranilate suitable for sulfate analysis.

The operating principle of the automated instrument may be briefly described as follows:

Solvent mobile phase (60% IPA) in reservoir (LR) is continuously fed through cation exchange (CX) and barium chloranilate (BC) columns at flow rates of about 3 ml/min by a high pressure liquid pump (LP). Background absorbance is continuously measured by a UV detector (D) at 310 nm and visually monitored in a strip chart recorder. A solenoid actuated, air operated switching valve (SV) is used for filling the external sampling loop (L) with samples in conjunction with an automatic sampler (AS) and peristaltic pump (PP) and injecting the samples into the columns. At CX cations are removed and at BC color reaction takes place. The $BaSO_4$ precipitate is retained in BC while the acid chloranilate is carried by the mobile phase through the detector system for colorimetric measurement.

For an automated sampling system such as shown in Figure 1, both SV and PP are electrically coupled to AS and controlled by electric timer relays such that both are activated whenever AS is sampling (i.e. L is being filled and mobile phase bypasses L). At the end of the sampling cycle, PP and AS stop and SV switches to the injection mode (i.e. mobile phase passes through L and carries the sample through CX and BC columns).

For manual operation, SV may be retained or replaced by a similar switching valve equipped with an extended handle for manual switching. Samples may be introduced into the sampling loop by syringe injection or by peristaltic pump system similar to the one used in the automated version.

The automatic sampler (AS) used in our system is a Technicon AutoAnalyzer sampler with turntable capacity of 40 sample cuvettes. The cam programmer was replaced by two digital timers to allow flexibility in setting cycle times for the sampling-rinse operations.

Analytical Operation

Before the start of an analytical run, all components are switched to the operating mode, and SV, AS, and PP are allowed to cycle normally to clean out all components. During this time the sampling probe is immersed in a large reservoir of 60% IPA to prevent introduction of air into the system. Analysis of the samples can proceed once a stable background absorbance is obtained. Sample cuvettes are filled with sample extracts and blank solutions (60% IPA) and then covered with thin polyethylene film to prevent evaporation losses. The filled cuvettes are arranged in the turntable according to the pattern blank, blank, sample, blank, blank for concentrated samples and blank, sample, blank for dilute samples. Blanks are used to wash out the system between samples and minimize sample overlap. Depending on the size of the sampling loop and the mobile phase flow rate, cycle time can vary from 2.5 to 6 minutes per sample or blank.

Calculation

A series of sulfuric acid standards in 60% IPA is normally run in the same manner as the samples, and a calibration curve, peak height vs. concentration, is plotted. Sample sulfate concentrations are calculated from the calibration curve. Total soluble sulfates in the filter $[SO_4^=]_F$ are calculated using the relation:

$$[SO_4^=]_F = (\mu g\ SO_4^=/ml) \times V_o \times d$$

where: V_o = total volume of original sample extract

d = dilution factor

= 1 if original sample extract was not diluted to bring detector response within range of the calibration curve

Discussion

The solubilities of barium chloranilate and $BaSO_4$ vary with the isopropanol/water ratio in the mobile phase. A momentary imbalance in this ratio as a result of injection of a slug of sample or blank gives a negative background response if the injected slug is richer in isopropanol than the mobile phase, and a positive response if it is richer in water. To minimize this effect, both the extracting solvent and the mobile phase for the analytical runs should be taken from the same stock solution.

In order to determine the maximum absorbance of the acid chloranilate ions as they elute out of the barium chloranilate column of the automated system, the colored eluates corresponding to sulfate concentrations in the range 0 - 30 µg/ml were collected and scanned in a Cary 14 spectrophotometer. In this concentration range, peak maximum was observed at 312 nm. This almost coincides with the 310 nm isobestic point (absorbance independent of pH) reported by Schafer (3).

For isopropanol-water system, the volume of the mixture is not equal to the sum of original volumes of the individual components. In the case of a 60/40 isopropanol/water mixture, volume shrinkage on mixing is about 2.7%. This volume change should be taken into account when preparing standards or samples from aqueous solutions.

The working concentration range and sensitivity of the automated system depend on sample size. A degraded sensitivity better than 0.5 µg $SO_4^=$ per ml in 60% IPA was easily obtained using a 0.5 ml external sampling loop in conjunction with a duPont liquid chromatograph UV detector. Figure 2 shows a calibration run in the range 0-5 µg $SO_4^=$/ml using a 0,5 ml sampling loop with detector sensitivity set at 0.02 absorbance units full scale. The last two peaks, 4048 and 4048, correspond to exhaust samples from a noncatalyst car. Testing mode was the Federal Test Procedure. The calibration curve is non linear with concentration and becomes flatter at the low concentration end. This is strongly suggestive of interplay of thermodynamic and kinetic effects. Similar behavior was likewise observed at the high concentration end.

Table I shows the precision obtained for five repetitive scans of sulfate standards at concentrations of 1, 2, and 4 μg/ml using a 0.5 ml sampling loop. At this concentration range the standard deviation is ±.05 μg/ml.

Two experiments were conducted to determine the extractability of sulfuric acid from and absorption in Fluoropore filters. In the first of these, known amounts of sulfuric aicd in 60% IPA were deposited on the filters and allowed to dry overnight. The filters were then extracted with 60% IPA and the extract analyzed for sulfates after the filters equilibrated with the solution overnight. The second involved immersion of dry filters in standard solutions of sulfuric acid and analysis of the solution after overnight equilibration. The results show that extraction is quantitative and that the filter has practically no affinity for the solute. These results are summarized in Tables II and III.

Table IV shows the efficacy of the collection technique for trapping sulfuric acid aerosols. The aerosols were generated using a Collison aerosol generator, and then fed into the CVS dilution tunnel under conditions simulating a test run. The aerosols were collected through isokinetic probes and collected on Fluoropore filters. The back-up glass fiber filters used in these runs did not gain measurable weights, indicating no significant breakthrough of the collected particulate from the primary collecting filters.

Figure 3 shows a typical analytical scan of extracts from exhaust samples from cars run on nonleaded fuel. The first five peaks are sample peaks, while the next six are calibration peaks corresponding to concentration range 0-6 µg $SO_4^=$/ml. The last three samples were diluted tenfold to bring detector response within calibration range. As a general rule, calibration runs are always made for each series of samples, as peak height-concentration relation may change as flow rate, back pressure, and column permeability vary over an extended period. This practice may be dispensed with for systems equipped with integrators.

Table V shows typical results of analysis for soluble sulfates of nonleaded exhaust samples collected on Fluoropore filters using the Federal Test Procedure. The low sulfate results correspond to test runs with noncatalyst cars and the high results to test runs with catalyst equipped cars.

A few filter samples were analyzed sequentially by x-ray fluorescence technique and by the barium chloranilate method. The filters were first analyzed x-ray fluorescence, then extracted with 60% IPA and analyzed for sulfate in the automated instrument. The results are summarized in Table VI. Considering the fact that sample handling techniques were not closely monitored, agreement between the two methods is encouraging.

Conclusion

The automated method described in this report offers a sensitive (less than 0.5 µg $SO_4^{=}$ per ml), fast (less than four minutes throughput time from initial sample injection into the column), and convenient method for the analysis of soluble sulfates in auto exhaust. Sample preparation is minimal, as this involves only simple extraction with 60% IPA. There are no precipitates to cause deterioration of the optical cell, as the $BaSO_4$ precipitate is effectively retained in the barium chloranilate reactor column. Although primarily addressed to trace sulfate analysis of auto exhausts from cars run on nonleaded fuels, the method may be adapted to any sulfate sample which can be leached out with water or aqueous alcoholic solution.

Table I

Precision of Repetitive Measurements

	Peak Height		
[$SO_4^=$] in μg/ml	1	2	4
	9.7	21.2	47.8
	9.9	20.4	48.8
	9.6	21.2	49.5
	10.2	20.3	48.6
	8.8	21.2	49.0
Mean	9.6	20.9	48.7
Standard Deviation	± 0.5	± 0.5	± 0.6
Coefficient of Variation	5.2	2.4	1.2

Table II

Recovery of Deposited H_2SO_4 on Fluoropore Filters by Extraction with 60% IPA

Total µgs $SO_4^=$ on Filter	
Deposited	**Found**
10	10
20	20.5
30	30
40	40.5
50	50
60	60
169	172
338	350
507	494

Table III

Absorption of H_2SO_4 in 60% IPA by Fluoropore Filters

Total µgs $SO_4^=$ in Solution	
Initial	Final
10	10.5
20	20
40	40.8
60	61.2
200	205
400	392

Table IV

Collection of Generated H_2SO_4 Aerosols Fed into the CVS Dilution Tunnel

Sample #	Mass Loading in μgs	Total $SO_4^=$ on Filter in μgs	% $SO_4^=$ on Filter
4001-3	956	350	36.6
4002-4	1791	664	37.1
4003-2	1076	390	36.2
4004-1	1323	217	16.4
4005-3	2403	856	35.6
4006-3	296	115	38.8
4007-1	468	197	42.2
4008-2	21181	8438	39.8

Table V

Typical Results of Sulfate Analysis of Nonleaded Exhaust Samples Collected on Fluoropore Filters

Sample #	Mass Loading in μgs	Total $SO_4^=$ in μgs	% $SO_4^=$ as % Mass Loading
4034-1	415	20	4.8
4035-3	271	15.5	5.6
4036-3	252	16.7	6.6
4037-3	151	11	7.3
4038-3	120	10.8	9.0
4039-3	287	10.5	3.3
4076-3	232	84	36.2
4079-3	308	106	34.4
4080-3	430	192	44.6
4084-3	506	241	47.6
4087-3	765	316	41.3

Table VI

Soluble Sulfate Analysis: Preliminary Comparison of X-Ray Fluorescence and Barium Chloranilate Method (BCM)

Total $SO_4^=$ on Filters in μg

		X-Ray Fluorescence			
Sample #	Mass Loading	Low Resolution	High Resolution	BCM	Ratio X-Ray/BCM
4006	459	208	-	219	0.950
4007	379	184	-	173	1.064
4014	358	143	-	156	.917
4017	285	37	-	44	.841
4023	390	142	-	113	1.256
4032	1065	296	-	245	1.208
4036	224	-	12.8	9.8	1.306
4038	84	-	17.0	7.8	2.179
4039	250	-	12.4	9.8	1.265
4050	390	-	18.0	13.7	1.314

References

1. Bertolacini, R. J. and Barney, J. E., "Colorimetric Determination of Sulfate with Barium Chloranilate," Anal. Chem. 29, 281 (1957).

2. Ibid, "Ultraviolet Spectrophotometric Determination of Sulfate, Chloride, and Fluoride with Chloranilic Acid," Anal. Chem. 30, 202 (1958).

3. Schafer, H. N. S., "An Improved Spectrophotometric Method for the Determination of Sulfate with Barium Chloranilate as Applied to Coal Ash and Related Materials," Anal. Chem. 39, 1719 (1967).

4. Barton, S. C. and McAdie, H. G., "An Automated Instrument for Monitoring Ambient H_2SO_4 Aerosol," In Proceedings of the Third International Clean Air Congress, Dusseldorf, Federal Republic of Germany, 1973, VDI-Verlag Gmb H, 1973, p. C25.

5. Gales, M. E., Jr., Kaylor, W. H. and Longbottom, J. E., "Determination of Sulphate by Automatic Colorimetric Analysis," Analyst 93, 97 (1968).

FIGURE 1

FLOW SCHEMATIC FOR AUTOMATED SULFATE INSTRUMENT

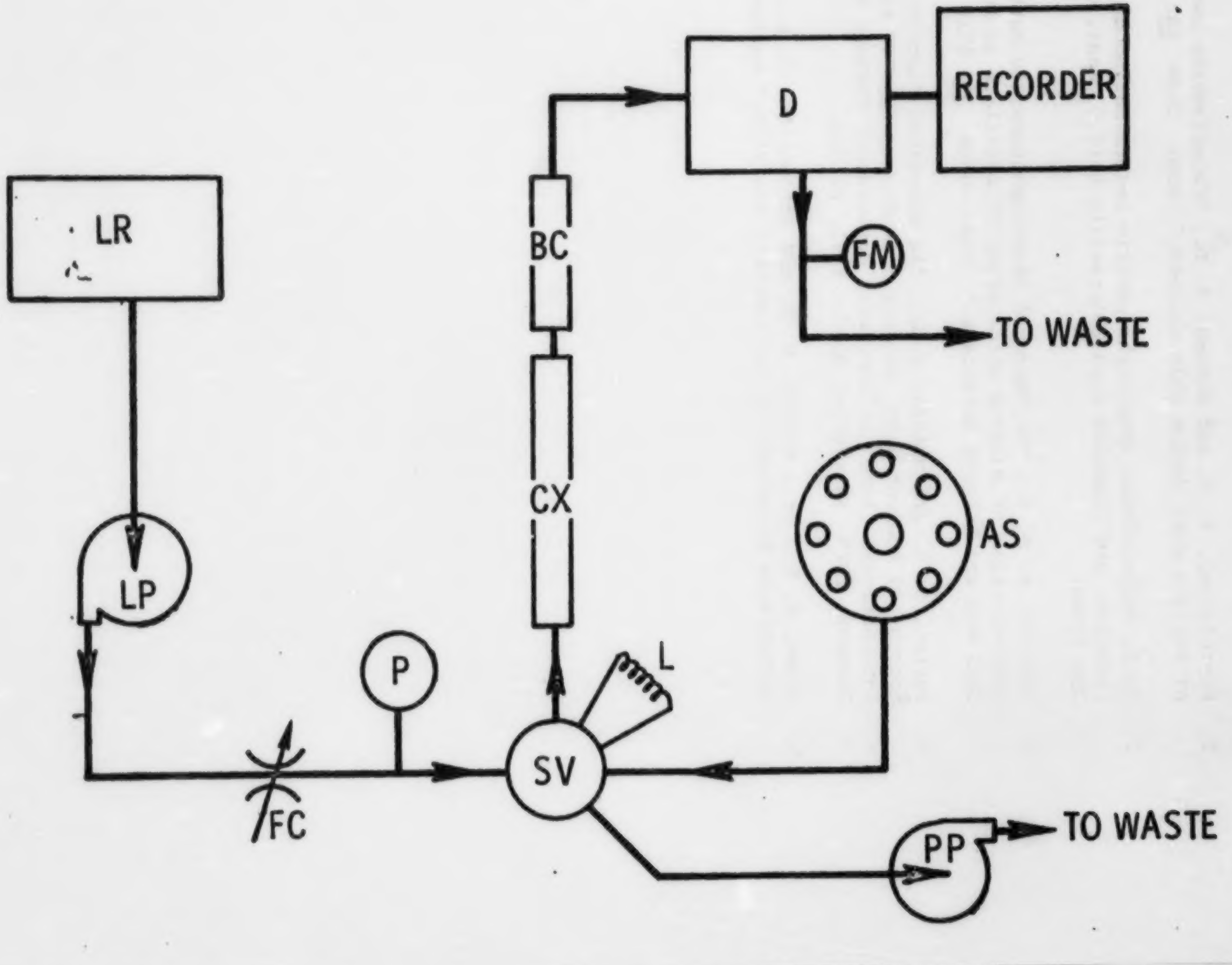
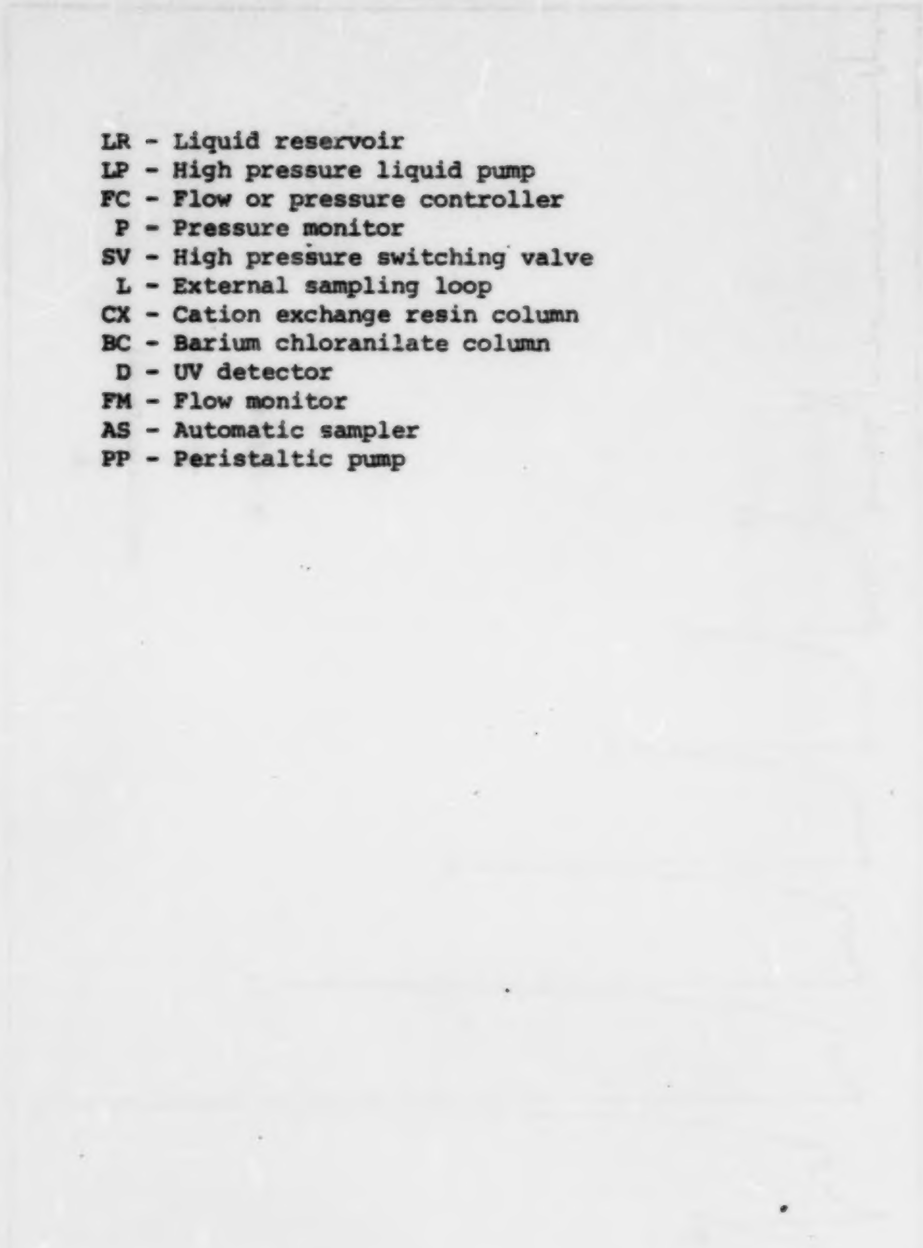

LR
LP
FC
P
SV
L
CX
BC
D
RECORDER
FM
TO WASTE
AS
PP
TO WASTE

Figure 1

Flow Schematic for Automated Sulfate Instrument



LR - Liquid reservoir
LP - High pressure liquid pump
FC - Flow or pressure controller
P - Pressure monitor
SV - High pressure switching valve
L - External sampling loop
CX - Cation exchange resin column
BC - Barium chloranilate column
D - UV detector
FM - Flow monitor
AS - Automatic sampler
PP - Peristaltic pump

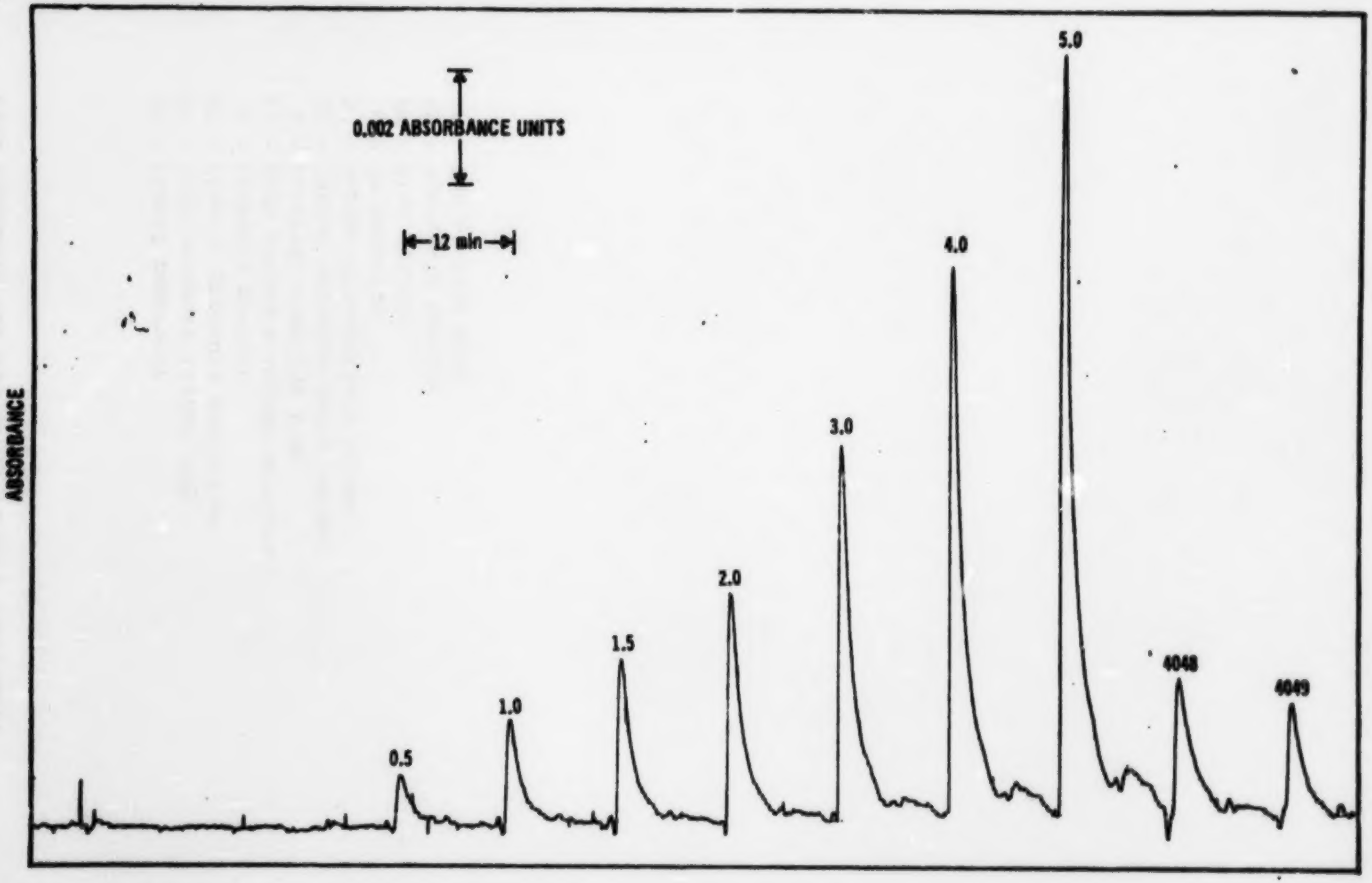

ABSORBANCE
0.002 ABSORBANCE UNITS
12 min
0.5
1.0
1.5
2.0
3.0
4.0
5.0
4048
4049

Figure 2

Sulfate calibration for concentration range 0-5 μg $SO_4^=$ per ml in 60% IPA. 4048 and 4049 are exhaust samples from a car not equipped with catalyst.

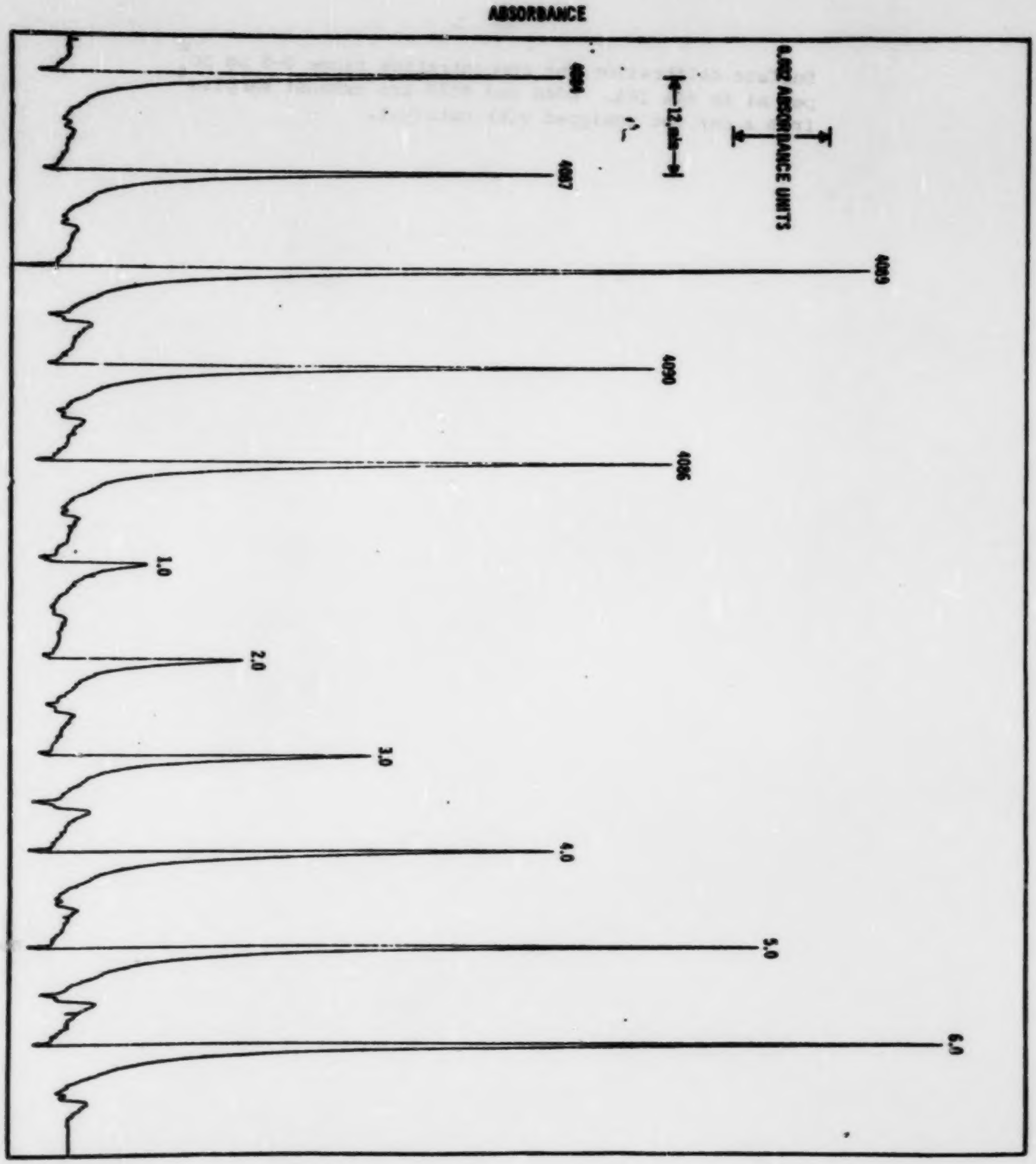


Figure 3. Typical scan of exhaust samples from catalyst equipped cars. Samples have been diluted to bring response within calibration range 0-6 μg $SO_4^=$/ml.

ENGINE ROOM DILUTION TUBE FLOW CHARACTERISTICS

BY

Robert L. Holden

Emissions Testing and Characterization Section
Chemistry and Physics Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina

National Environmental Research Center
Office of Research and Monitoring
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

September, 1974

ABSTRACT

This report describes work done to characterize gas flow and particulate flow in a dilution tunnel used in automotive emissions research. In addition to velocity profiles being graphically presented, a particulate profile study is also included. A description of some troubles and corrective measures is also reported. Finally, some qualitative statements, based on rough preliminary measurements, are reported on the subject of aerosol deposition and loss to the walls and bends of the engine exhaust pipe of our system.

ACKNOWLEDGMENTS

The author greatly appreciates the help and support of all his section coworkers. But special thanks is given to Dr. Ronald L. Bradow for suggesting the importance of this study and to Henry J. Becker whose help in fabricating necessary parts and carrying out the measurements was invaluable.

I. INTRODUCTION

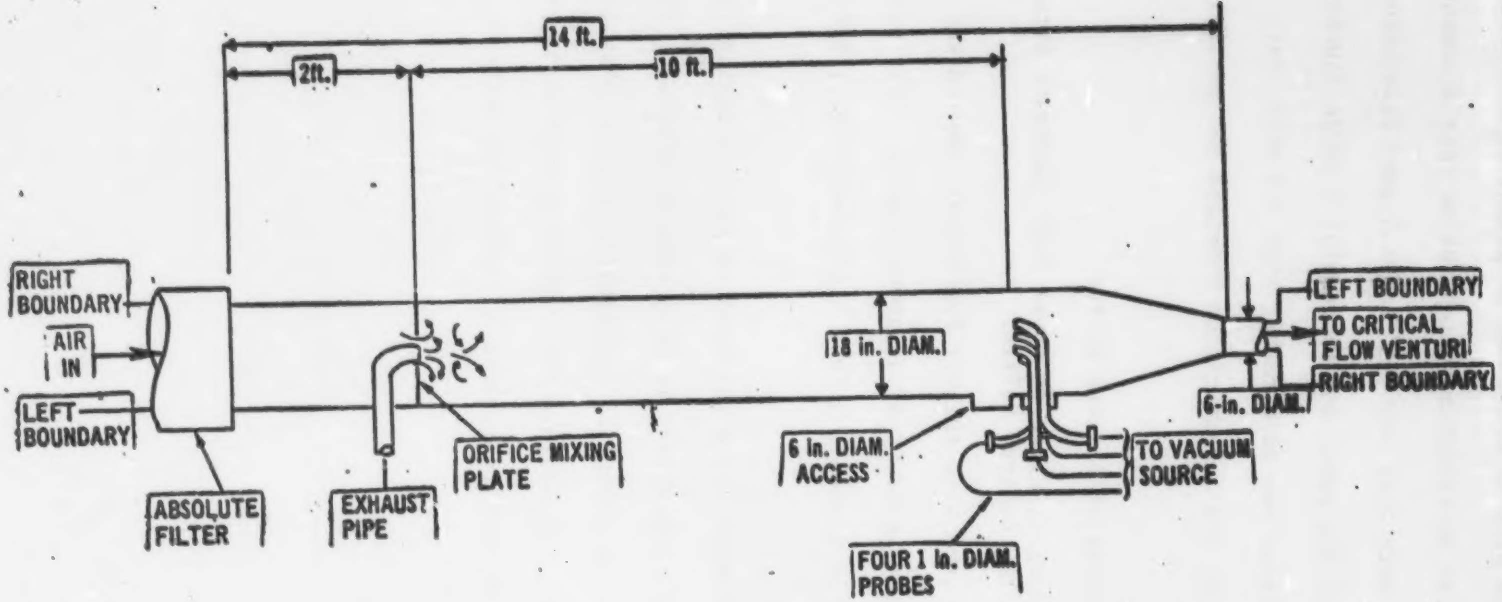
A series of experiments was conducted on the 18 inch diameter engine room dilution tube located at the Beaunit facility of EPA-NERC, Chemistry and Physics Laboratory. These experiments were designed to determine the velocity profile and aerosol particulate concentration profile for this dilution tube. In addition, some qualitative data on sulfate aerosol deposition and loss was obtained.

II. VELOCITY PROFILE

The purpose of these experiments was to determine if the velocity distribution of the tube is conducive to proportional sampling among the four filters of the probe rake which is placed at the down stream end of the tube (See Figure 1).

The measurements were made using a Thermo Systems Inc.* model 1054B anemometer and model 1210-60 hot film sensor. The air flow was produced by the tube exhaust blower. The sensor was placed approximately two inches in front of the sampling probes and was moved horizontally and vertically along lines passing through the tube center. Data was collected at one inch intervals, with no data taken closer than one inch from the tube edge (to prevent damage to the sensor). After the initial profile run, it was determined that some changes were in order and 2 more profiles were made.

*


14 ft.
2ft.
10 ft.
RIGHT BOUNDARY
AIR IN
LEFT BOUNDARY
ABSOLUTE FILTER
EXHAUST PIPE
ORIFICE MIXING PLATE
18 in. DIAM.
6 in. DIAM. ACCESS
FOUR 1 in. DIAM. PROBES
TO VACUUM SOURCE
6-in. DIAM.
LEFT BOUNDARY
TO CRITICAL FLOW VENTURI
RIGHT BOUNDARY

Side view of 18-inch dilution tunnel

The results of each profile are shown on graphs of horizontal distribution and vertical distribution which follow this discussion (See Figures 2, 3, 4, &5). Note that test "A" shows higher flow velocity in the top left quadrant of the tube, and in general a large fluctuation across the tube (turbulence was also rather high for this test). This was deemed unsatisfactory and investigation revealed two possible problem areas:

(1) incomplete filling of air bag filter

(2) large open spaces (located in upper left quadrant) between tube boundary and flow control baffle.

Test "B" was conducted with the air bag filter removed and the baffle sealed to the tube boundary by silicone sealer. This produced a relatively smooth profile across the tube (turbulence still present, but reduced somewhat).

Test "C" was performed with a absolute filter of negligible pressure drop in place of the air bag filter (baffle remains sealed). This again produced a relatively flat (about 5% fluctuation across tube) profile with reduced turbulence. We believe this velocity profile to be satisfactory for aerosol data collection by filtration methods.

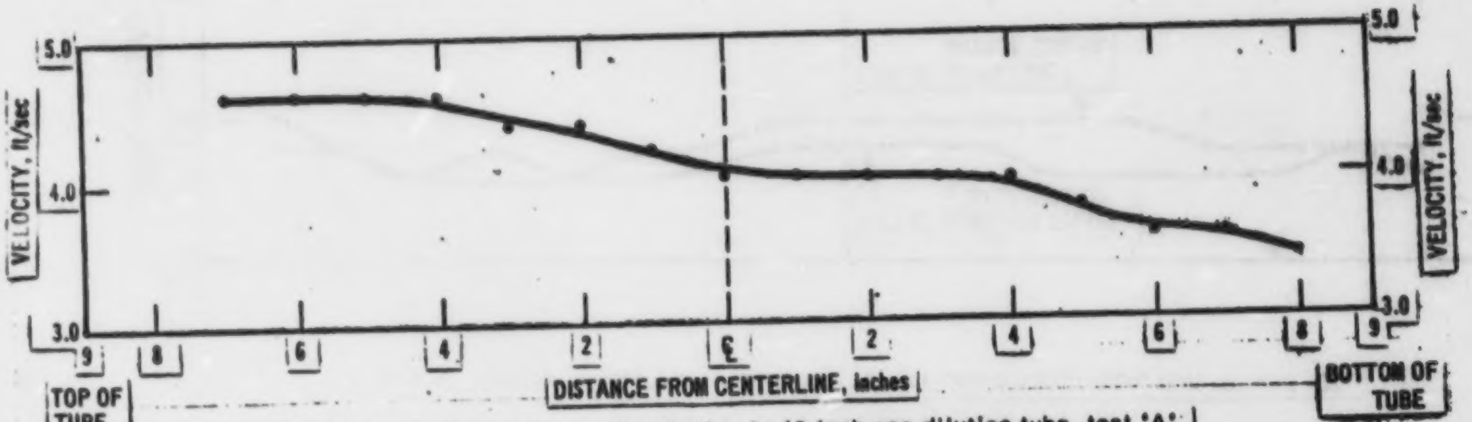


Figure 2. Vertical velocity distribution in 18-inch gas dilution tube, test 'A'.

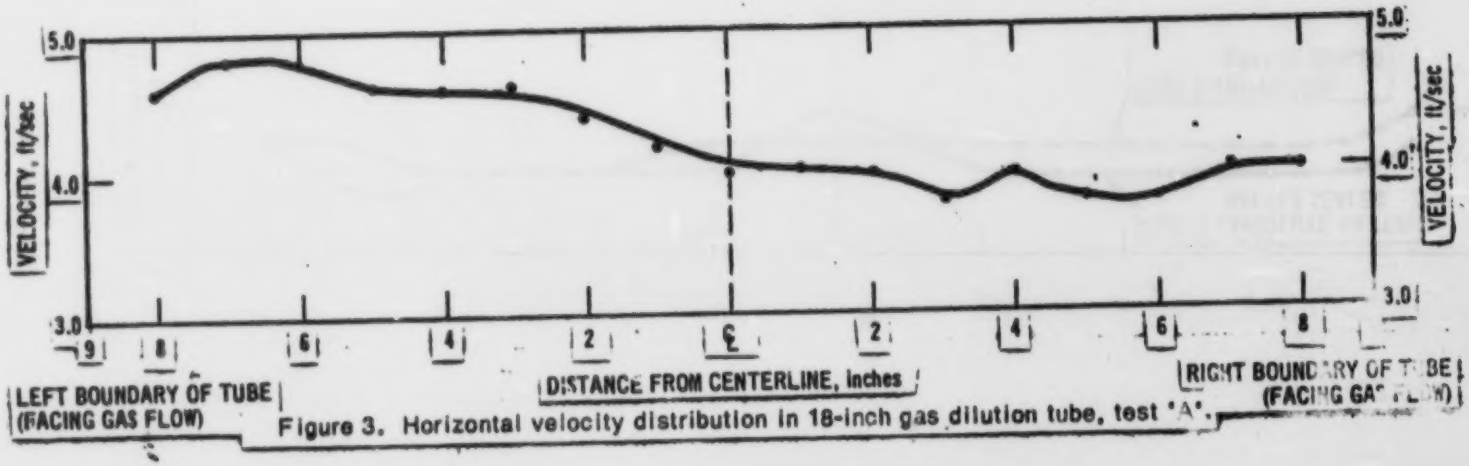


Figure 3. Horizontal velocity distribution in 18-inch gas dilution tube, test 'A'.

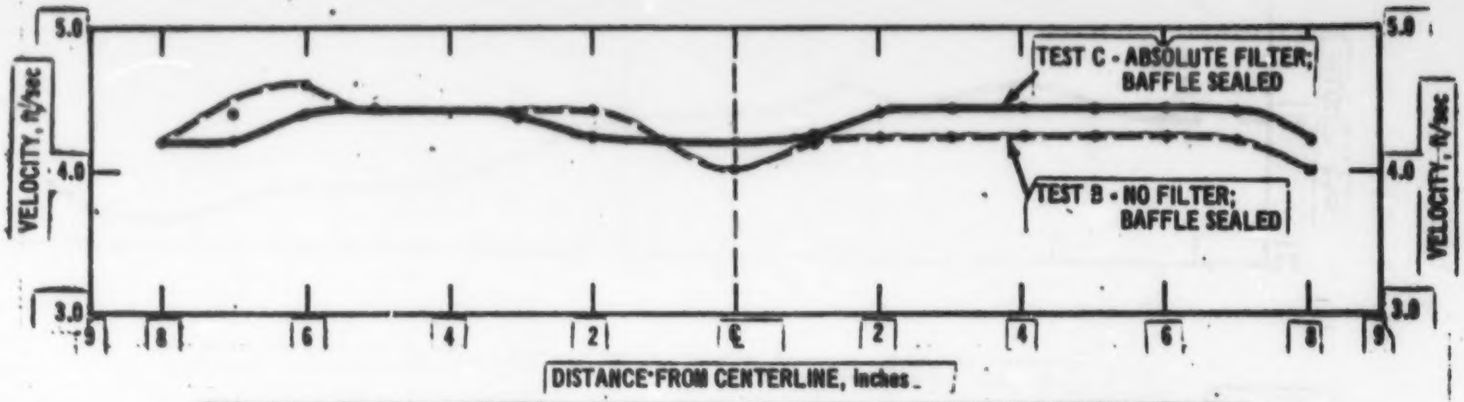


Figure 4. Vertical velocity distribution in 18-inch gas dilution tube, test 'B' and 'C'.

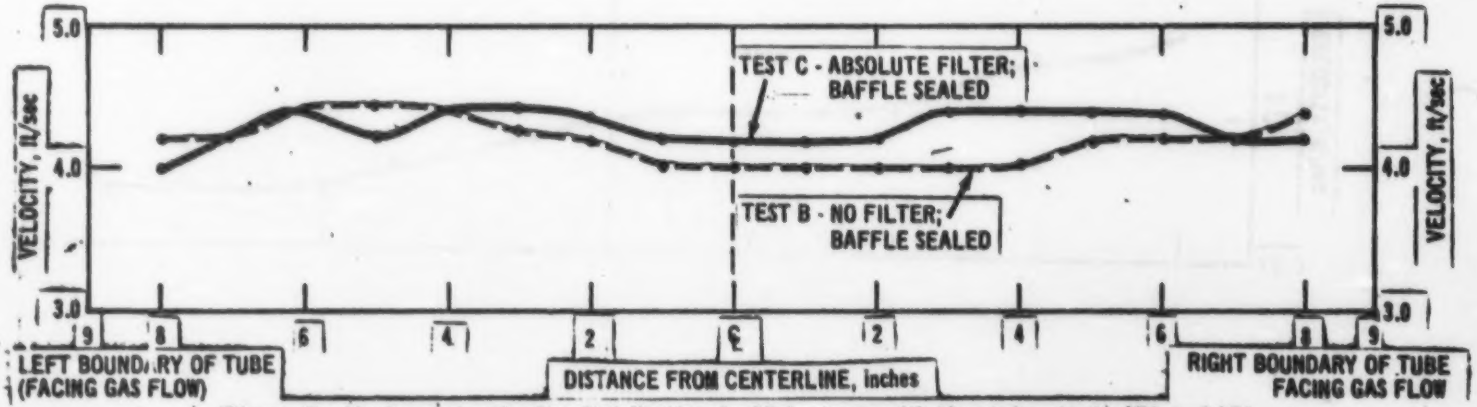


Figure 5. Horizontal velocity distribution in 18-inch gas dilution tube, tests 'B' and 'C'.

III. AEROSOL FLOW PROFILE

The purpose of this group of experiments is to examine the mass concentration profile of aerosols carried down the tube by air flow from the exhaust blower unit. The information obtained from these experiments allows us to determine if the aerosol follows the gas flow uniformly or if it collects in certain areas of the tube cross section .

A model 7300 aerosol generator from Environmental Research Corporation was used to generate a sulfuric acid mist from a 10% solution of the acid. The aerosol flow rate was 49 liters per minute which corresponds to a mass generation rate of approximately 1.04 grams per minute. The mist was then injected into the dilution tube at the point where the engine exhaust pipe opens in the tube. As in the velocity profile tests, the dilution tube exhaust blower created an air flow which carried the aerosol through the tube. Note that the engine was not operating during any of these tests.

The aerosol was sampled by a one inch diameter stainless steel probe drawn across the tube horizontally and vertically (passing through the center). Figures 6 and 7 illustrate the sampling points. The aerosol was drawn into the sampling probes by a vacuum flow of one cfm, and was then collected on teflon fluoropore filters of 47 mm diameter. Each sampling run lasted 30 minutes.

The results of the experiments are shown in figures 6 and 7. This data indicates that the aerosol mass concentration profile is relatively smooth and uniform (at least to the limits of reproducible massing

6.

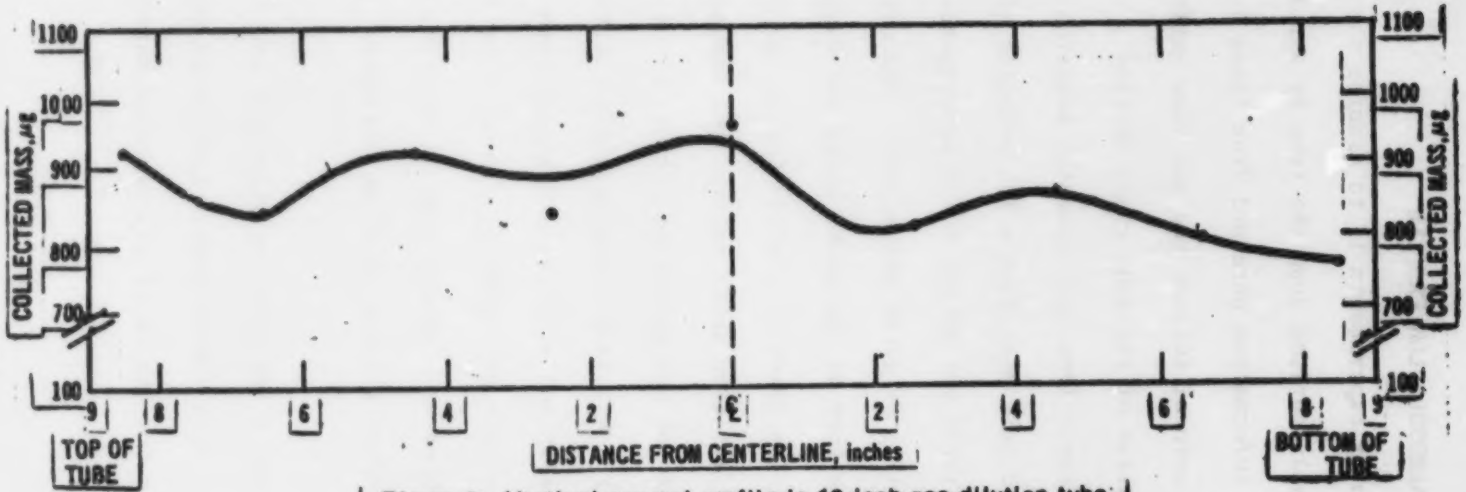


Figure 6. Vertical aerosol profile in 18-inch gas dilution tube.

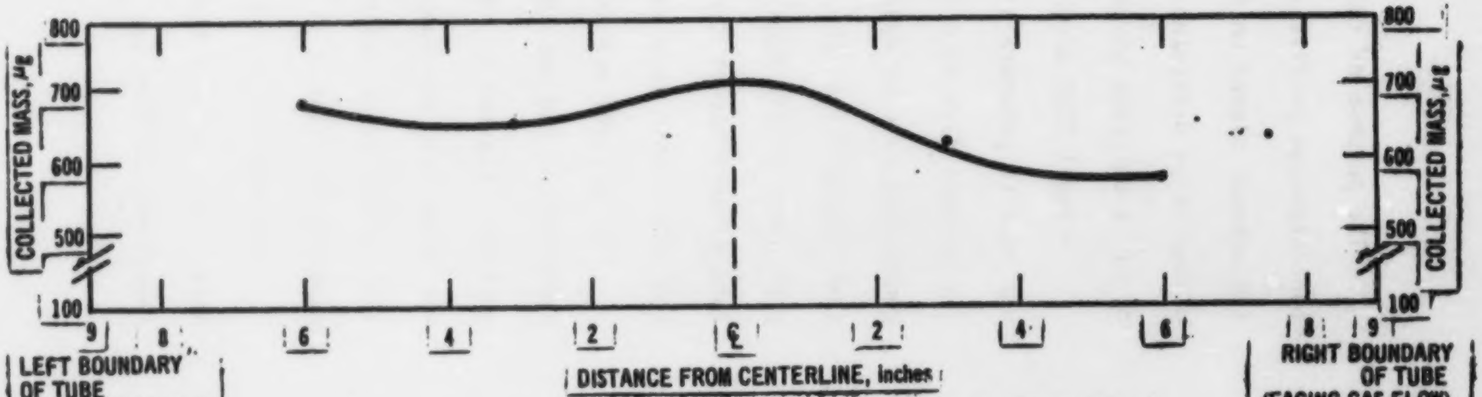


Figure 7. Horizontal aerosol profile in 18-inch gas dilution tube.

accuracy with a microbalance). An independent chemical massing analysis performed on the filters confirms this uniformity, and we are convinced that the aerosol follows the gas flow and will be sampled representatively by the four-probe sampling rake at the end of the tube.

To examine the possibility of aerosol loss due to engine exhaust pipe interception of the mist, the aerosol was injected just inside the exhaust pipe so that it had to travel through four feet of 2 inch diameter pipe with one right angle bend. The aerosol was sampled by the four-probe rake (which is in the center 4 inches of the tube) and collected on 47 mm fluoropore filters. The results (shown in Table 1 below) indicate, qualitatively at least, that there could be a 10% to 20% aerosol loss to the exhaust pipe walls and bends. Thus, before sulfate studies are carried out, one should test this loss possibility and make corrections to data if necessary.

TABLE 1

PROBE #	DIRECT INJECTION: AVERAGE MASS COLLECTED (μ grams)	INJECTION INTO EXHAUST PIPE: AVERAGE MASS COLLECTED (μ grams)
1	718	592
2	483	422
3	958	764
4	518	468

NOTES: (1) averages taken over three runs.

AN EPA AUTOMOBILE EMISSIONS LABORATORY
RESEARCH TRIANGLE PARK, NORTH CAROLINA

by

Peter A. Gabele
Ronald L. Bradow
Chemistry and Physics Laboratory
Research Triangle Park, North Carolina

ABSTRACT

This report describes the establishment of an exhaust emissions laboratory where gaseous emissions can be analyzed in accordance with the 1975 Federal Test Procedure (FTP) and particulate emissions are conditioned for sampling in dilution tunnels. The effect of fuel additives, catalysts, and other pertainent variables on the character of both gaseous and particulate emissions are examined in this laboratory.

The paper discusses the measures taken on the test stand to attain simulation of a vehicular engine when operating over a specified driving cycle. Test equipment, experimental apparatus, data analyses methods, data reducing methods, and calibration and evaluation measures of significance are described. The results of a comprehensive aerosol study on the 18 inch diameter dilution tunnel are provided which include velocity and concentration profiles and information on particle deposition within the tunnel.

SECTION I

INTRODUCTION

PURPOSE

Concern has been leveled at the extent and character of particulate emissions from internal combustion engines. Much of the work accomplished to date has dealt primarily with the effect of lead anti-knock and lead scavenger additives on exhaust emissions.(1,2) More recently emphasis has been placed on characterizing particulate emissions from engines which are equipped with catalysts. The effect of fuel additives upon these emissions is also in need of investigation. Therefore, project personnel have endeavored to establish an engine-dynamometer test facility having a particulate sampling capability. The particulate sampling function does not interfere in any way with the ability to sample exhaust gases in accordance with the 1975 Federal Test Procedure.(3)

Particulate matter exhausted from automobiles is defined as any material, other than unbound water, which condenses at 90°F into particles larger than a small molecule, but smaller than 500 microns in diameter. These emissions are of concern because particulate matter suspended in air has been designated by EPA as a criteria pollutant for which ambient air quality standards are required. Compliance with these standards mandates the development of emission control regulations which eventually may apply to automobiles.

SCOPE

In order to compare project findings with results from chassis dynamometer studies, test stand engines must closely simulate actual vehicular engine operation. This requirement specifies such things as test engine type, engine parameter settings, test cycles, and mechanisms for properly loading the engine. In short, loads and speeds of the test stand engine must follow as closely as possible those of that engine when operated in a vehicle over an identical test cycle. The extent to which simulation is being carried out should be determined once the set up becomes operational.

Design and development of a particulate sampling apparatus is required. Representative samples must be collected in a form which can be readily analyzed for composition and weight. The sampling system must be evaluated to determine the extent to which a representative sample is being collected.

The flexibility of being able to examine different engines, test cycles, catalysts, and fuels and fuel additives is necessary. Operation of the Constant Volume Samplers at various dilution ratios is also necessary.

All system variables of ordinary interest should be either continuously monitored or easily obtainable. For this purpose a comprehensive temperature measuring, indicating, and recording system is necessary. Also, such things as engine and dynamometer torque, sample flowrates, etc., should be displayed on gauge boards or console indicators.

Two independent gasoline engine-dynamometer systems are required to provide sufficient experimental data consistent with project goals. Both engines should be capable of simultaneous, continuous, and automatic operation. This requirement is imperative for mileage accumulation purposes.

A data reduction system must be developed to reduce emissions information. This system must be easily accessible and capable of yielding rapid results. Emissions of hydrocarbons, carbon monoxide, and nitrogen oxides must be reduced to units of grams per mile in accordance with the 1975 Federal Test Procedure.

PROJECT OUTLINE

DESIGN AND CONSTRUCTION PHASE

The design and construction phases of the test facility included the installation and, in some cases, design and calibration of the following:

1. an engine dynamometer bedplate,
2. two eddy current dynamometers,
3. two engines,
4. two dilution tunnels,
5. two constant volume sampler (CVS) systems,
6. particulate sample probe rakes and filter holders,
7. engine transmission to dynamometer couplings,
8. lube oil and fresh water cooling systems,
9. flywheel inertia weights,
10. temperature indicating and logging system,
11. programmable cycle driver.

Replacement of various outdated dynamometer indicating and control instrumentation was also accomplished in the design work.

Design of the dilution tunnels and associated sampling equipment is of vital importance to the validity of the experiments at hand. Figure 1 shows a schematic of the dilution tunnel geometry for one test engine set up; Fig. 2 shows the other tunnel. For ease in future identification of these two systems, the 4 inch and the 18 inch diameter tunnels will hereafter be referred to in connection with X system and Y system, respectively.

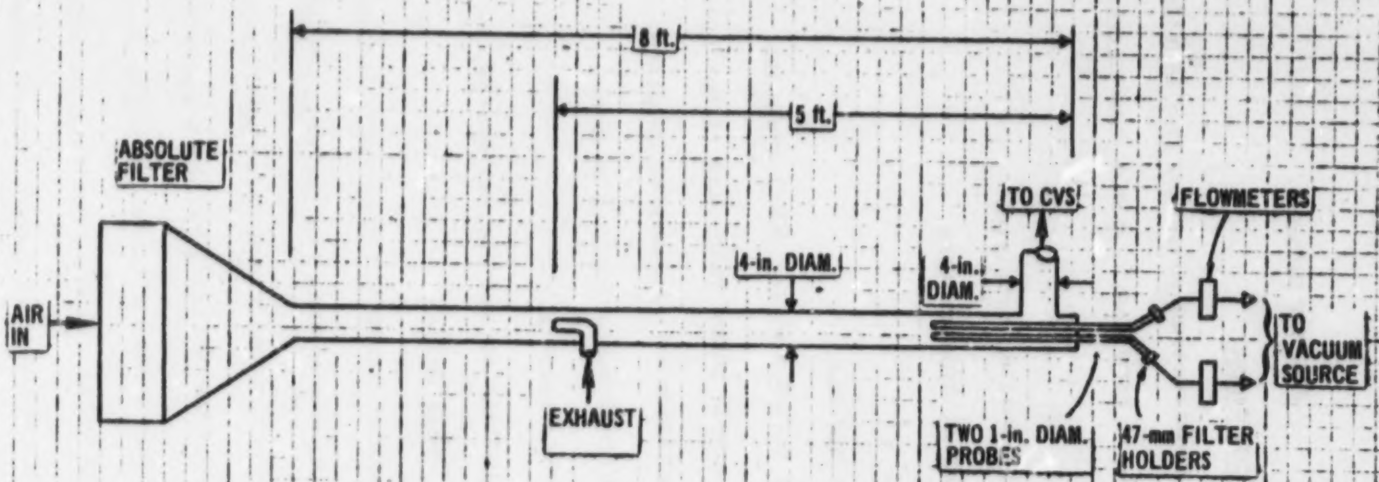

8 ft.
5 ft.
ABSOLUTE FILTER
TO CVS
FLOWMETERS
4-in. DIAM.
4-in. DIAM.
AIR IN
TO VACUUM SOURCE
EXHAUST
TWO 1-in. DIAM. PROBES
47-mm FILTER HOLDERS

FIG. 1

Side view of 4-inch dilution tunnel.

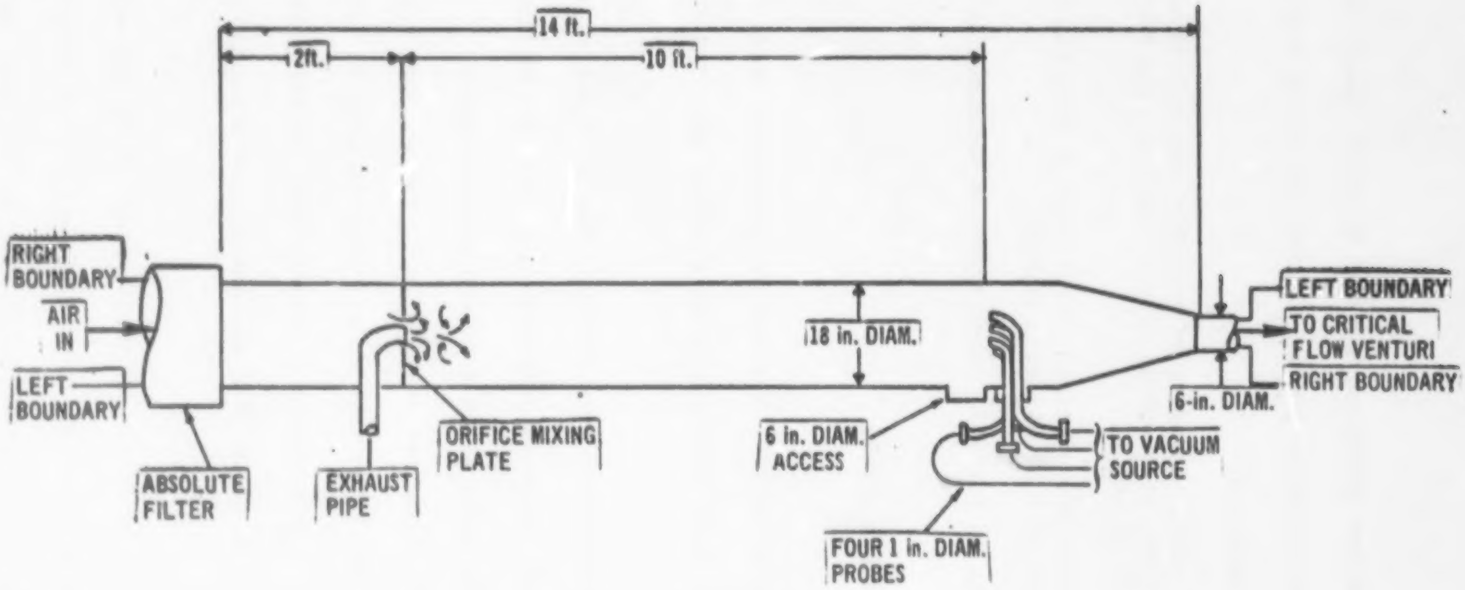

14 ft.
2ft.
10 ft.
RIGHT BOUNDARY
AIR IN
LEFT BOUNDARY
ABSOLUTE FILTER
EXHAUST PIPE
ORIFICE MIXING PLATE
18 in. DIAM.
6 in. DIAM. ACCESS
FOUR 1 in. DIAM. PROBES
TO VACUUM SOURCE
6-in. DIAM.
LEFT BOUNDARY
TO CRITICAL FLOW VENTURI
RIGHT BOUNDARY

Fig. 2. Side view of 18-inch dilution tunnel

EVALUATION PHASE

Test stand engine operation and the dilution tunnel required evaluation for qualification purposes. The following evaluation procedures were conducted:

1. The test stand engine speed-manifold vacuum traces and exhaust gas emissions were compared with those of the vehicle on the chassis dynamometer.
2. Gas velocity and particle concentration profiles were examined inside the 18 inch dilution tunnel.
3. The extent of particle deposition was examined in both dilution tunnels.

CONSTRUCTION AND DESIGN PHASE

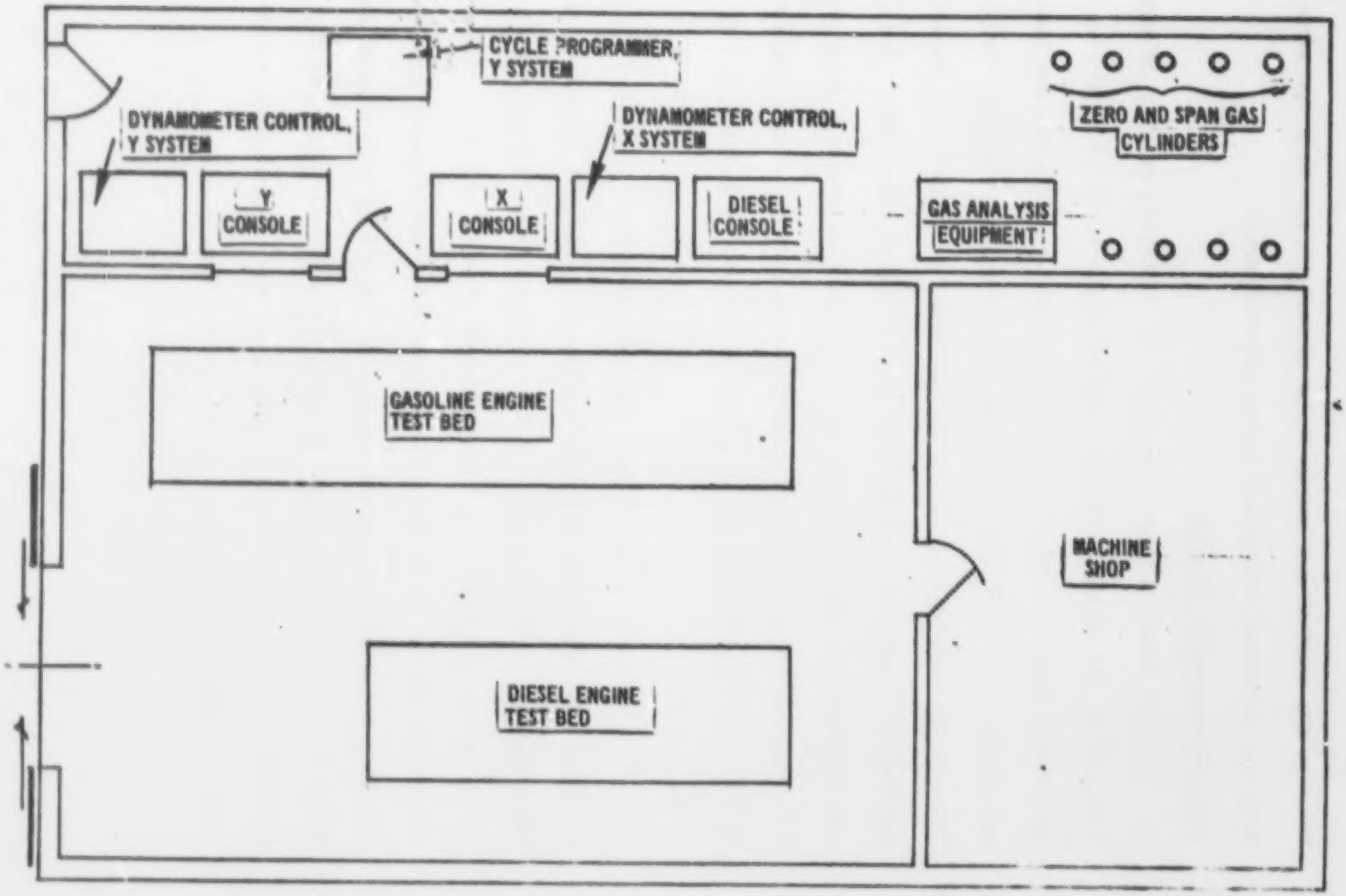
General Layout

The plan drawing in Fig. 3 shows two principal areas wherein the project is concentrated--the engine-dynamometer room and the analysis-control room.

The engine-dynamometer area contains two gasoline engine-dynamometer combinations, two dilution tunnels, two constant volume samplers, and, eventually, a diesel test stand and particulate sampler.

To achieve good sampling results, both temperature and humidity control are necessary. Ten tons of air conditioning is available to the project area for this purpose. Temperature in the engine-dynamometer room are controlled to about 72°F and humidities are maintained below 65%.

The analysis control room contains three engine dynamometer consoles, two cycle programmers, a NO-NO_x chemiluminescent analyzer, one NDIR CO_2 and two NDIR CO analyzers, one FID hydrocarbon analyzer, and an



CYCLE PROGRAMMER, Y SYSTEM
ZERO AND SPAN GAS CYLINDERS
DYNAMOMETER CONTROL, Y SYSTEM
DYNAMOMETER CONTROL, X SYSTEM
Y CONSOLE
X CONSOLE
DIESEL CONSOLE
GAS ANALYSIS EQUIPMENT
GASOLINE ENGINE TEST BED
MACHINE SHOP
DIESEL ENGINE TEST BED

FIG. 3 Plan view of project area.

automatically sequencing three bag sampling system. Windows between the control and engine rooms permit closed door operation with all personnel stationed in the control area.

Engine-Dynamometer Stands

Initial construction began with the installation of a 20 ton, 5 ft. by 20 ft. steel bedplate. The bedplate rests on a 10-inch thick reinforced concrete floor. Holes have been drilled into the concrete and anchor bolts are used to secure the bedplate in place. Isopads between the bedplate and floor are arranged to effectively isolate any bedplate vibrations generated during engine operation. The engines and dynamometers are oriented on the bedplate as shown in Fig. 4. Both engines may be operated independently, however, when run simultaneously, gas emissions from only one engine can be sampled at any one time.

The engines are 1972 model, 350 CID, Chevrolet Impalas. Both are equipped with 2-barrel Rochester carburetors and 350 turbohydramatic transmissions. These engines and transmissions are identical to those installed in the Chevrolet test vehicles at this facility. Engine oil and water are cooled in heat exchangers which are plumbed into the building water system. Water thermostat valves on the engines have been retained and are set to maintain water temperature below 195°F. Transmission oil is cooled in a fin type, air cooled, heat exchanger with a 12 volt automobile air conditioning fan.

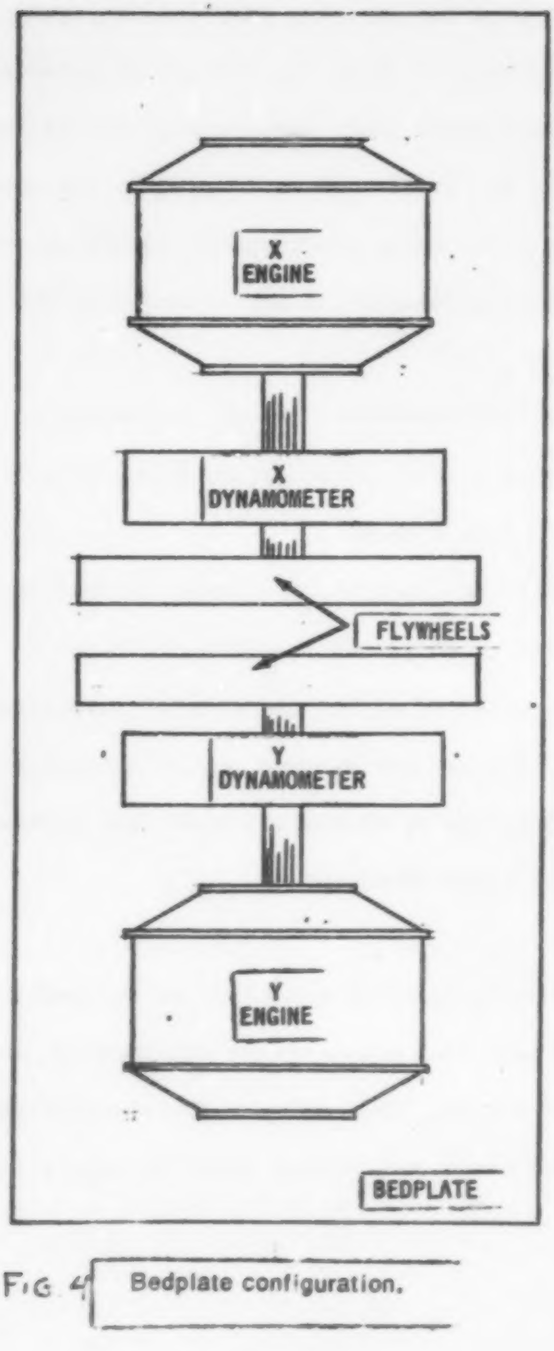

X
ENGINE
X
DYNAMOMETER
FLYWHEELS
Y
DYNAMOMETER
Y
ENGINE
BEDPLATE

FIG. 4 Bedplate configuration.

A 55 gallon drum located outside the building for safety reasons supplies fuel to the engines. Fuel additives can be added, mixed, and set into place on the supply line within minutes. This arrangement, however, has precluded the use of fuel evaporative cannisters.

The engine-dynamometers are dry gap, eddy current types manufactured by Eaton Dynamatic. Both are absorption rated at 175 hp. Dynamometer cooling water temperature, rpm, current excitation level, and torque are displayed on console guages located in the control room.

The dynamometer controls apply loads to the engine by controlling excitation current to the dynamometer in accordance with two different modes:

1. Speed Control: The excitation current is varied as necessary to hold the engine at a selected speed providing, of course, the throttle is sufficiently opened.
2. Current Control: The excitation current is held constant while the speed is allowed to vary with throttle position.

These modes may be selected either manually or automatically during operation. For example, the dynamometer controls are programmed to automatically switch to the speed control mode when braking the engine during periods of rapid deceleration.

Engine Control Features

Each engine has been equipped with a throttle control actuator which is part of the closed loop servo system designed to control engine throttle from a program source. The engine-throttle-actuator system is set up to control the servo loop around speed by utilizing a rate and value feedback from the engine. On the Y engine an additional rate feedback is obtained from a manifold vacuum transducer for stabilization purposes.

Each engine is inertially loaded by utilizing a flywheel which is keyed to the dynamometer shaft. The total inertia load on the engine is calculated as a composite of the dynamometer rotor, couplings, and flywheel inertia weights. This is 306 and 508 units for X and Y systems, respectively. The required inertia loading based on a vehicle weight of 4500 lb. is 793.4 units. This inertia deficit has been compensated for in the Y engine system by programming loads into the dynamometer during periods of acceleration. Unfortunately, with an eddy current dynamometer there is no way of putting energy back into the engine, therefore, coast-down decelerations with the installed system tend to be higher than normal. This tendency is illustrated in Figure 5 wherein a comparison between coast-downs of the vehicle and X engine are compared. Although the disparity between these results is obvious, from an emission standpoint the error induced because of this is probably negligible when operating over the EPA Urban Driving Schedule.

Engine Calibrations

Various steps were performed in order to simulate actual vehicular operation. Carburetors were adjusted to attain the proper air-fuel mixtures by measuring exhaust gas content until it reached 0.5% CO and 2.5% O_2 levels (slightly lean of stoichiometric during idle). The programable inertia load was adjusted until a wide open throttle (WOT) acceleration from 0 to 50 mph in 8.0 seconds was recorded. This corresponded with the WOT acceleration on the vehicle. Excitation to

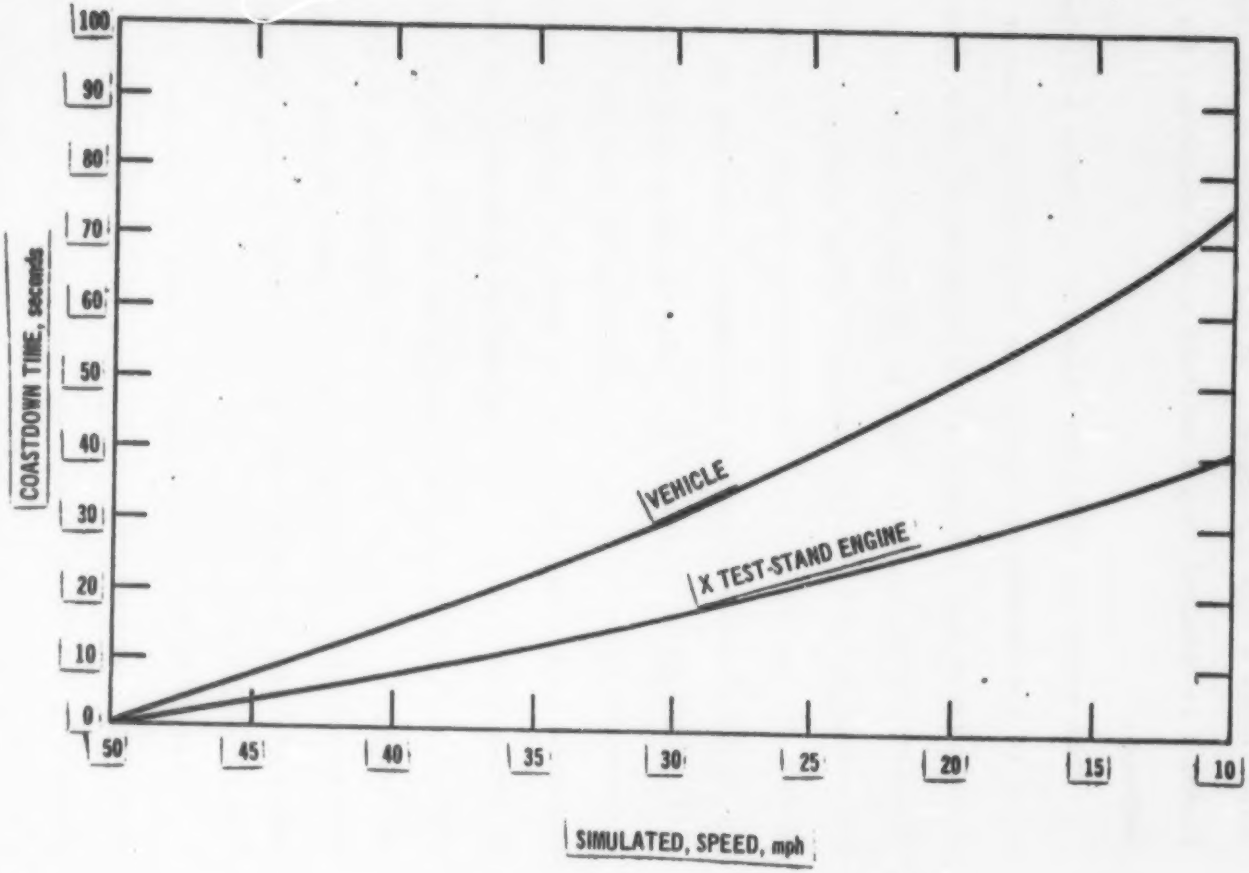


Fig. 5 Coastdown time for vehicle and X test-stand engine.

the engine dynamometers was adjusted such that the 50 mph level road load corresponded with that of the vehicular engine on the chassis dynamometer. Manifold vacuums were used in matching engine loads. The excitation necessary to match level road loads at speeds other than 50 mph approximated closely the 9 percent level required at 50 mph (see Fig. 6). Therefore, an excitation of 9 per cent is set into the dynamometer during steady cruise periods when the dynamometer is in current control mode.

Dilution Tunnels and Constant Volume Samplers

Both engines exhaust into dilution tunnels. The dilution tunnels and their associated sampling equipment are fabricated from stainless steel. The X system tunnel was designed by Esso Research and Engineering Company to measure vehicle particulate emissions. (4) The Y system tunnel, although designed by project personnel, is similar to a 16 inch tunnel which was developed by The Dow Chemical Company. (5)

For sampling particulate matter, the Y system tunnel has a four probe rake and the X system tunnel has a two probe rake. All probes are made from a one inch diameter stainless steel tubing. Each probe is connected to a vacuum source through a 47mm filter holder, a flowmeter, and a regulating valve. Flowrates are maintained at 1 ACFM throughout a test.

The 4 inch diameter tunnel (X system) is connected to a CVS which utilizes a roots blower as the constant volume source. The 18 inch diameter tunnel (Y system) utilizes a critical flow venturi as its constant volume source. Flowrates in both systems (see Figs. 7 and 3)

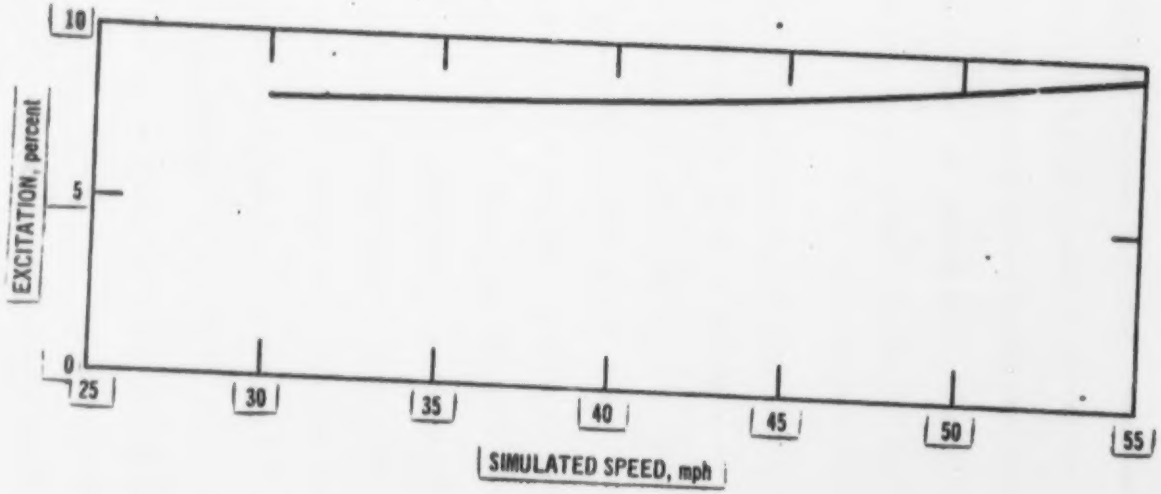


Fig 6 Current excitation required to simulate level road load of vehicular engine.

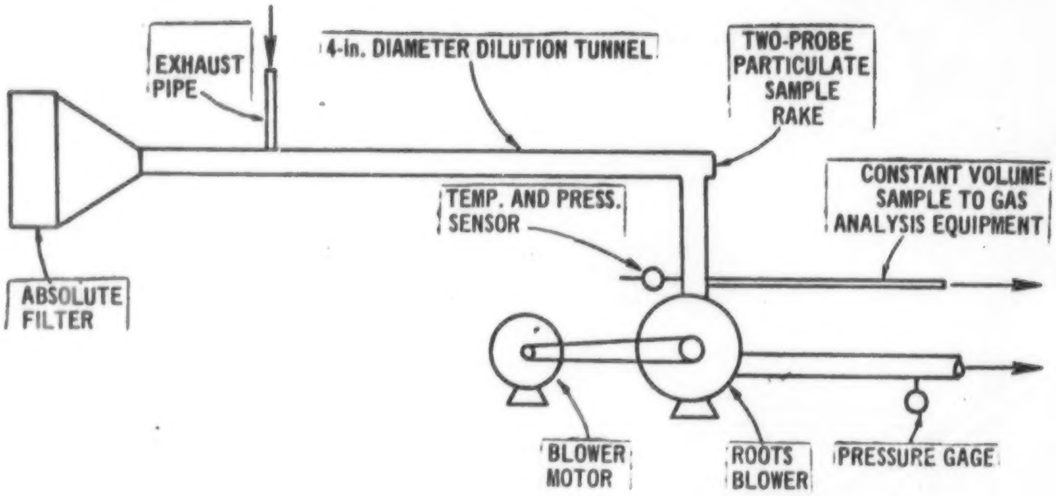

EXHAUST PIPE
4-in. DIAMETER DILUTION TUNNEL
TWO-PROBE PARTICULATE SAMPLE RAKE
CONSTANT VOLUME SAMPLE TO GAS ANALYSIS EQUIPMENT
TEMP. AND PRESS. SENSOR
ABSOLUTE FILTER
BLOWER MOTOR
ROOTS BLOWER
PRESSURE GAGE

Fig 7 X system dilution tunnel and CVS arrangement.

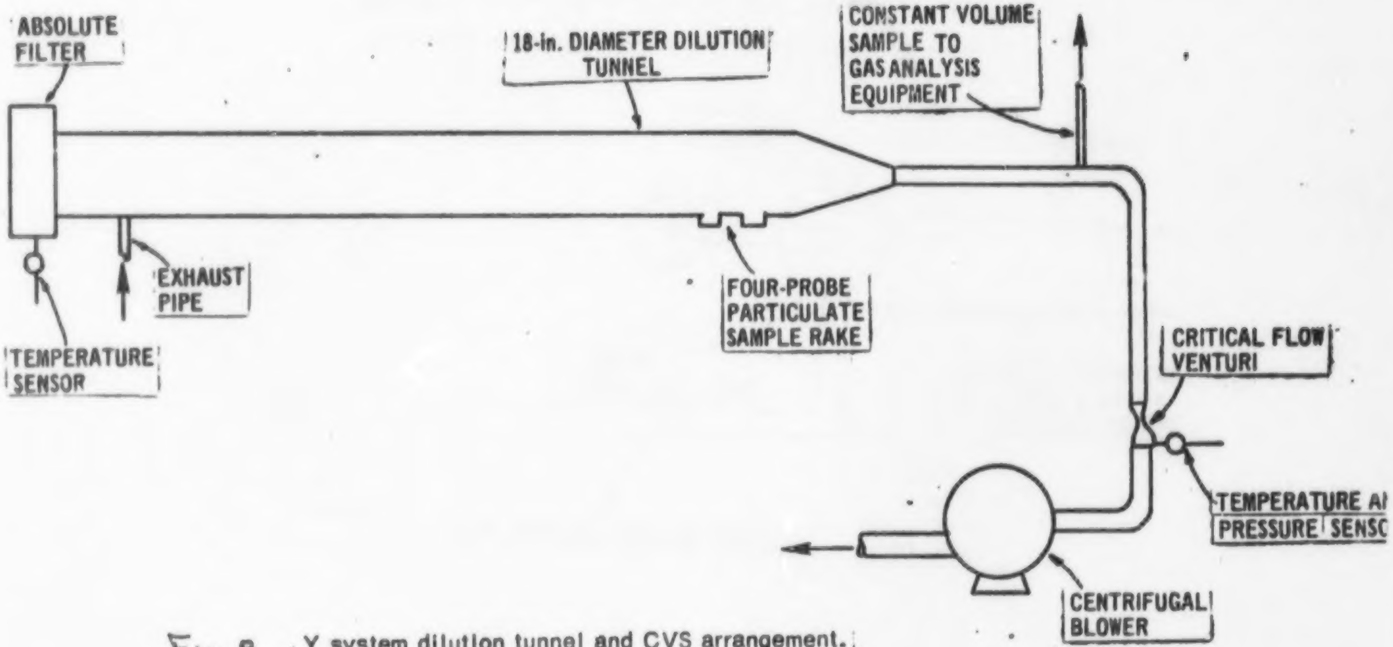

ABSOLUTE FILTER
18-in. DIAMETER DILUTION TUNNEL
CONSTANT VOLUME SAMPLE TO GAS ANALYSIS EQUIPMENT
TEMPERATURE SENSOR
EXHAUST PIPE
FOUR-PROBE PARTICULATE SAMPLE RAKE
CRITICAL FLOW VENTURI
TEMPERATURE A
PRESSURE SENSC
CENTRIFUGAL BLOWER

Fig. 8 Y system dilution tunnel and CVS arrangement.

can be varied by changing either drive belt pulley diameters in the X system or venturi sizes in the Y system. Once the system is set, total gas flowrate through the tunnels is determined by inducing a known quantity of propane into the system over a given period of time. The concentrations of propane in dilution air are determined using FID analyzer on a bag sample. Actual flowrate, Q, is calculated by the formula:

$$Q = \frac{(M)\ (22.4)\ (35.315)\ (10^{-3})}{(t)\ (c/10^{6})\ (44.1)}$$

M = mass in grams of propane injected
t = time in seconds over which test is carried out
c = concentration of propane in ppm

constants = 22.4 l/mole
$35.315\ \frac{ft^3}{m^3}$
44.1 g/mole C_3H_8
10^{-3} m3/1

Flowrates for the X system and Y system are 342 and 432 ACFM, respectively. Since the Y system employs a critical flow venturi as its method of maintaining a constant flowrate, the actual flowrate will vary slightly with pressure and temperature changes according to the relationship:

$Q = CP/\sqrt{T}$
P = pressure at the venturi entrance
T = temperature at the venturi entrance
C = constant

Because pressure changes in the installed system do not vary significantly during operation, only temperature changes require monitoring in order to correctly determine actual venturi flowrates. This function is fulfilled by temperature indicating system. Temperatures at the inlet to the roots blower on the X system CVS are likewise monitored. In both systems the temperatures are used to correct actual flowrates to standard values when calculating exhaust emissions.

Emission Analysis and Reduction

Both gaseous and particulate emission information is sought. Gaseous emissions are reported in accordance with the 1975 FTP. In addition, levels of fifty-five (55) individual hydrocarbons are measured using gas chromatographic techniques almost identical to those reported by Dimitriades and Seizinger (6). Energy dispersive x-ray fluorescence spectroscopy (7) is used to perform trace metal analysis on particulate matter. Particulates are also catalogued using a scanning electron microscope. SO_2 is determined by an adaptation of the method of West and Gaeke (8) and sulfate analysis are conducted using an automated colorimetric procedure involving the reaction of sulfate ions with the solid barium salt of chloranilic acid.(9)

Presently, data reduction for gaseous emissions is accomplished through a PDP-12 computer. Programs to compute emissions of hydrocarbons, CO, and NO_x in grams per mile, and fuel economy in miles per gallon, are stored on magnetic tape. Two of these programs in FOCAL-12 language are listed in Appendix A.

EVALUATION PHASE

Evaluation of the engine dynamometer set up was conducted to determine how closely the engines were simulating actual engine operation in a vehicle. An experimental program was also developed to evaluate the velocity and particle concentration profile in the plane of the sample probe inlets.

Engine manifold vacuum traces were recorded over the EPA Urban Driving Schedule (LA 4-5-3). The records for both test stand engines and the vehicular engine are shown in Figs. 9-11. X system engine displays consistently higher manifold vacuums when compared with the other two engines. Comparison between the Y system engine and the vehicular engine is good and indicated that both of these engines are experiencing approximately equal loads. Prior to recording all traces, engine manifold vacuums were observed equal under steady state 50 mph cruise conditions. Therefore, the differences seen in the traces are due primarily to the differences in inertia loadings. X system engine's high overall manifold vacuum is easily explained by citing its undersized flywheel for which compensation has not yet been made.

Other expected differences appear when comparing exhaust emissions reported over the EPA Urban Driving Schedule. Emissions are shown in Figure 12. The X system engine exhausts consistently lower NO_x emissions because it is experiencing lower combustion temperatures. Again the cause is the lower inertia loading experienced by the engine during acceleration.

Both velocity and particle concentration profiles were determined in the probe plane of the 18 inch dilution tunnel. Actual determination of profiles for the 4 inch tunnel is physically complicated by the small tunnel diameter, however, a strong theoretical argument supporting the contention that uniform profiles exist in the cross section of the tunnel has been developed by Esso Research.(4) Although sample flowrates at both tunnels was maintained at 1 CFM; only in the Y system can this be said to approximate an isokinetic condition for obvious reasons.

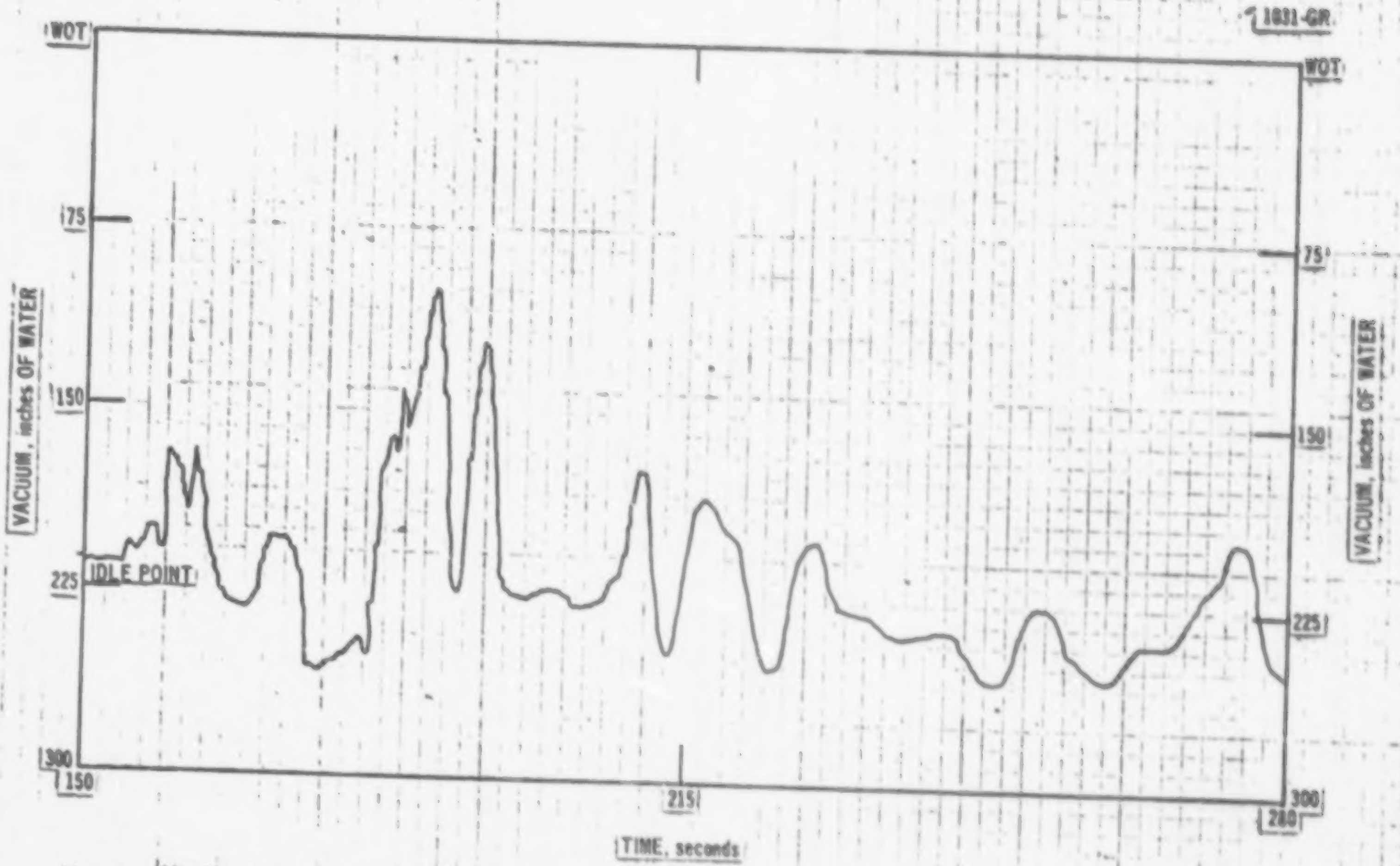


Fig 9 Manifold vacuum trace for X test stand engine from the 160 to 280 sec. mark on LA-4-54 cycle.

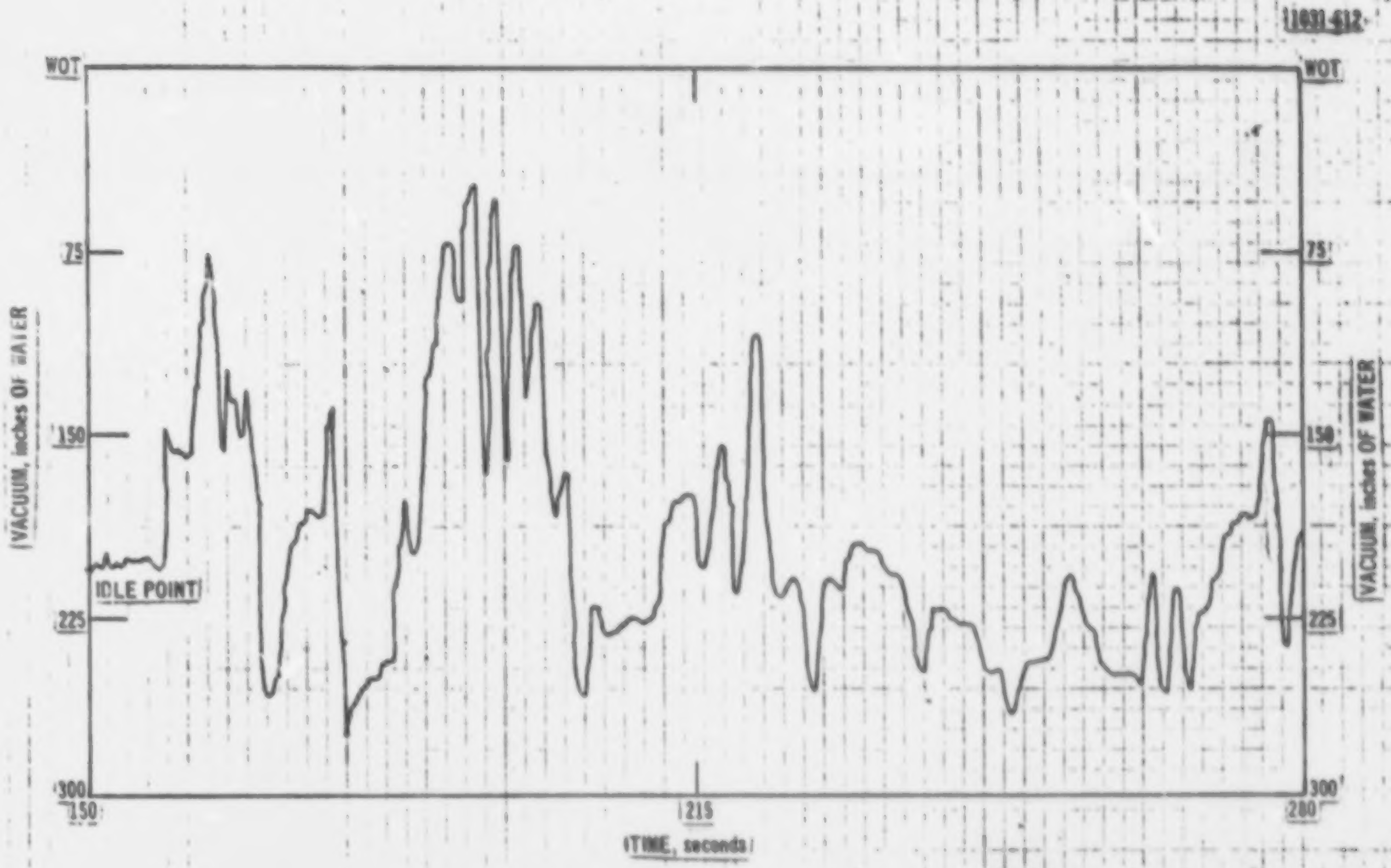


Fig. 10 Manifold vacuum trace taken for Y test-stand engine from the 150 sec. to 280 sec. mark on LA-4-5-4 cycle.

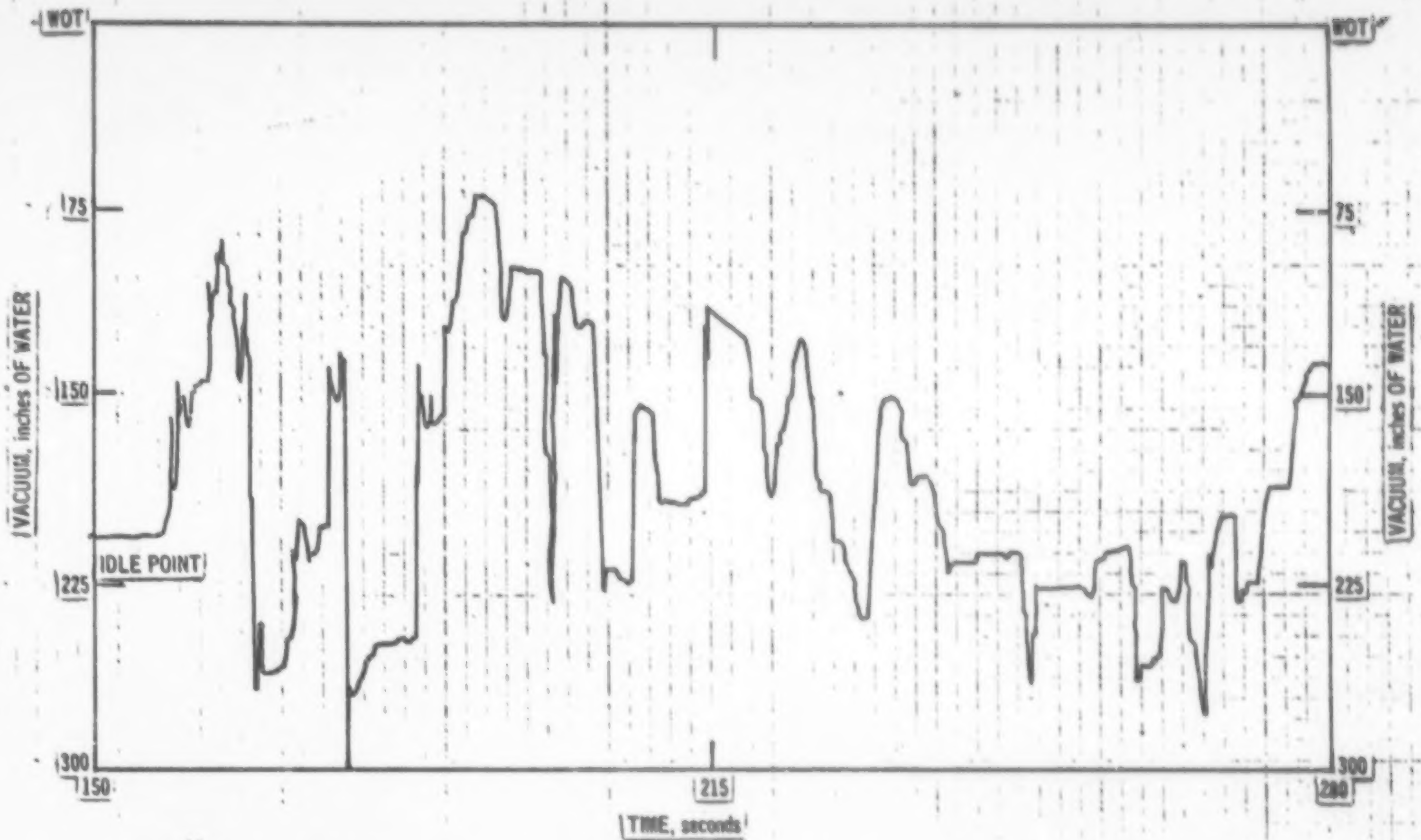


Figure ~~8~~ 11. Manifold vacuum trace taken for vehicular engine from 150 sec. to 280 sec. mark on LA-4-S-4 cycle.

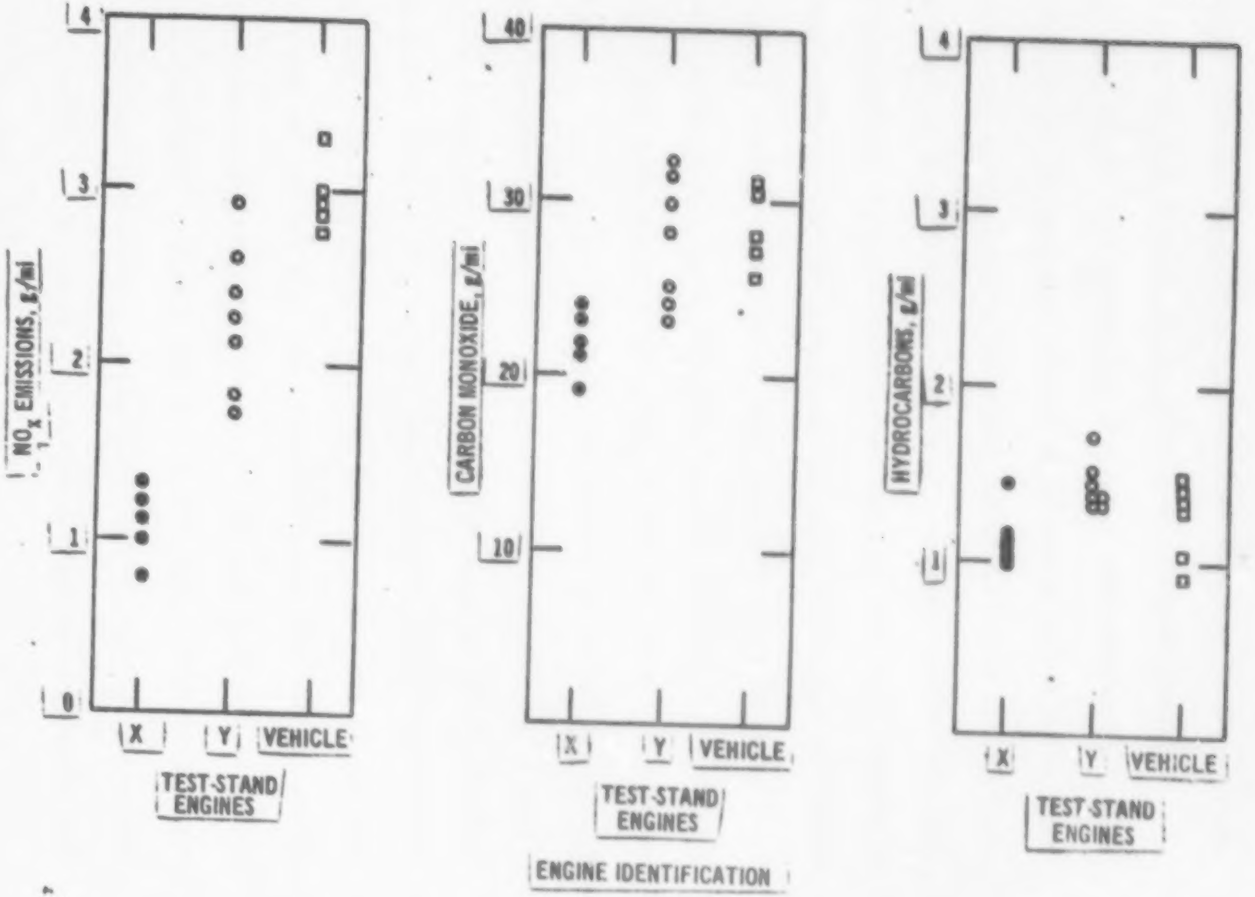


Fig. 12 Comparison of emissions for x and y test-stand and vehicular engines.

Because exhaust gas particles are generally below 3 microns, their behavior is much like that of a gas. For this reason the importance of sampling isokinetically becomes somewhat academic.

Velocity profiles were determined both horizontally and vertically while traversing with a thin film anemometer. Initially, traverses were performed with bag-type filters upstream of the tunnel. Profiles constructed for these runs indicated a non-uniform velocity situation and, therefore, absolute filters were substituted in their place. Traverses with and without the absolute filter upstream of the dilution tunnel resulted in the rather uniform profiles shown in Fig.13-14.

Concentration profiles were established using a sample probe and fluoropore filter to sample particles generated by a Collison particle generator. A 10 percent solution of sulfuric acid was dispersed by the generator as an aerosol having a particle size range from 0.03 to 3 microns. A 1 inch sample probe was traversed and particles sampled through the probe were collected on a teflon fluoropore filter. Each traverse point was sampled for 30 minutes and the sample flowrate was held at 1 CFM. Following collection, the filter weight was determined both by weighing and by wet chemical analysis of H_2SO_4 content on the filters. Both determinations agreed reasonably well. The horizontal and vertical concentration profiles are shown in Figs.15-16. The profiles indicate that particles are well mixed and evenly distributed in the plane of the probe rake.

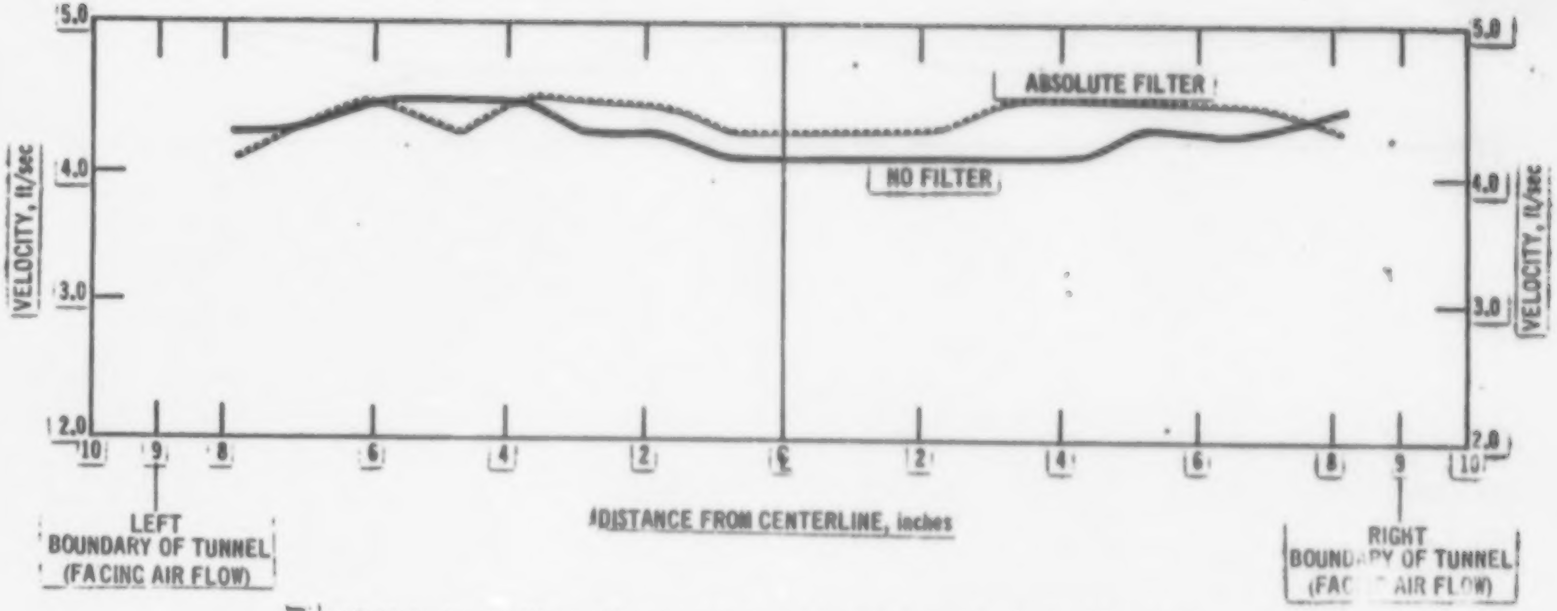


Fig. 13 Velocity profile on Y system dilution tunnel during horizontal traverse.

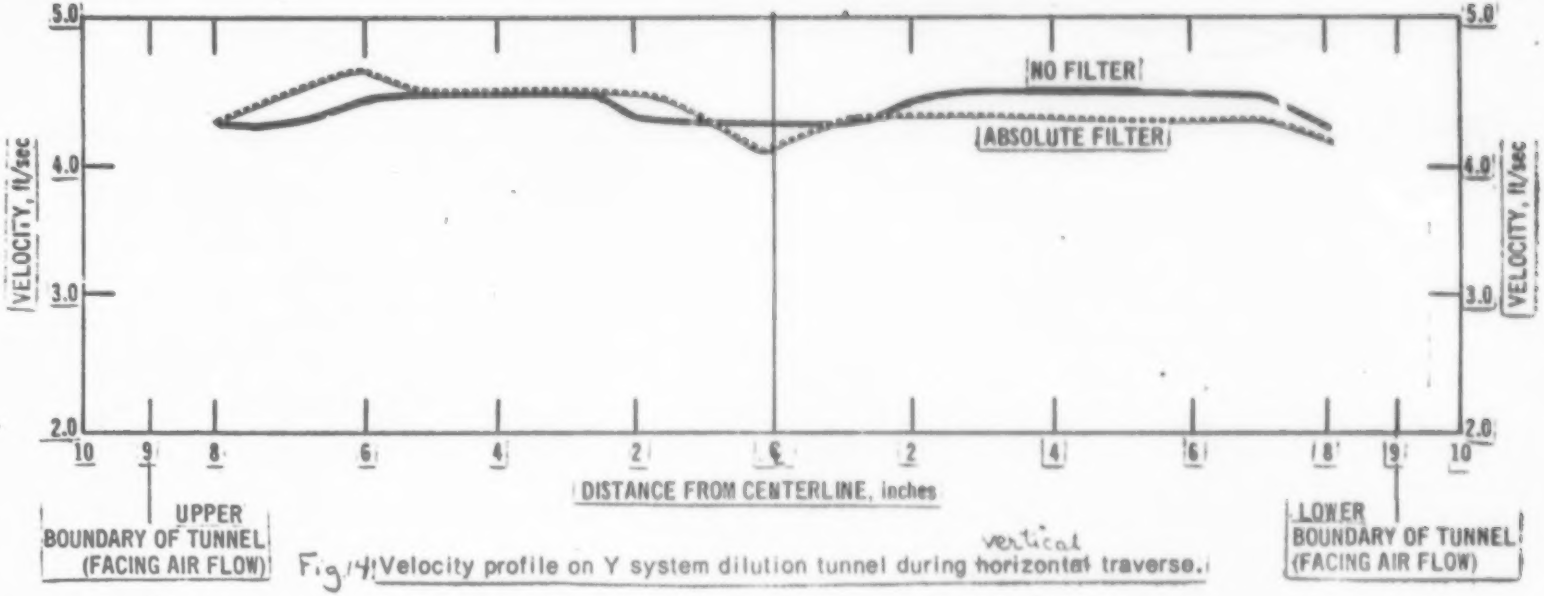


Fig. 4 Velocity profile on Y system dilution tunnel during vertical ~~horizontal~~ traverse.

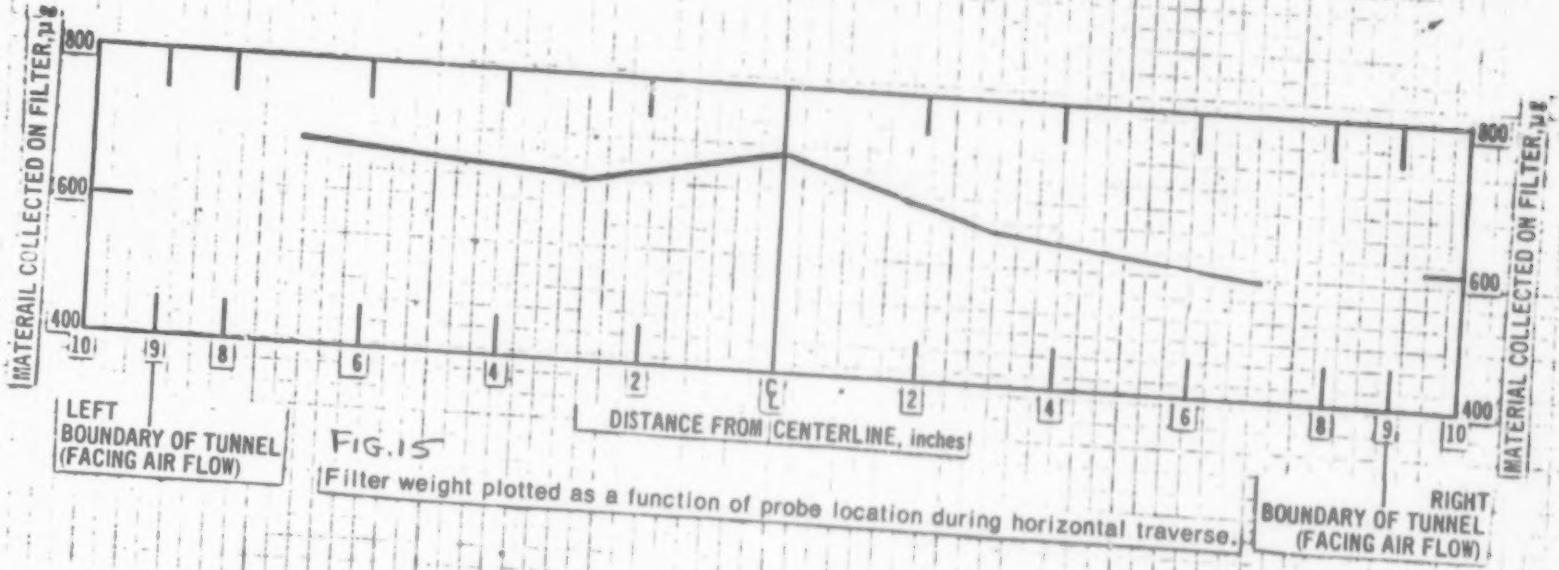


FIG. 15

Filter weight plotted as a function of probe location during horizontal traverse.

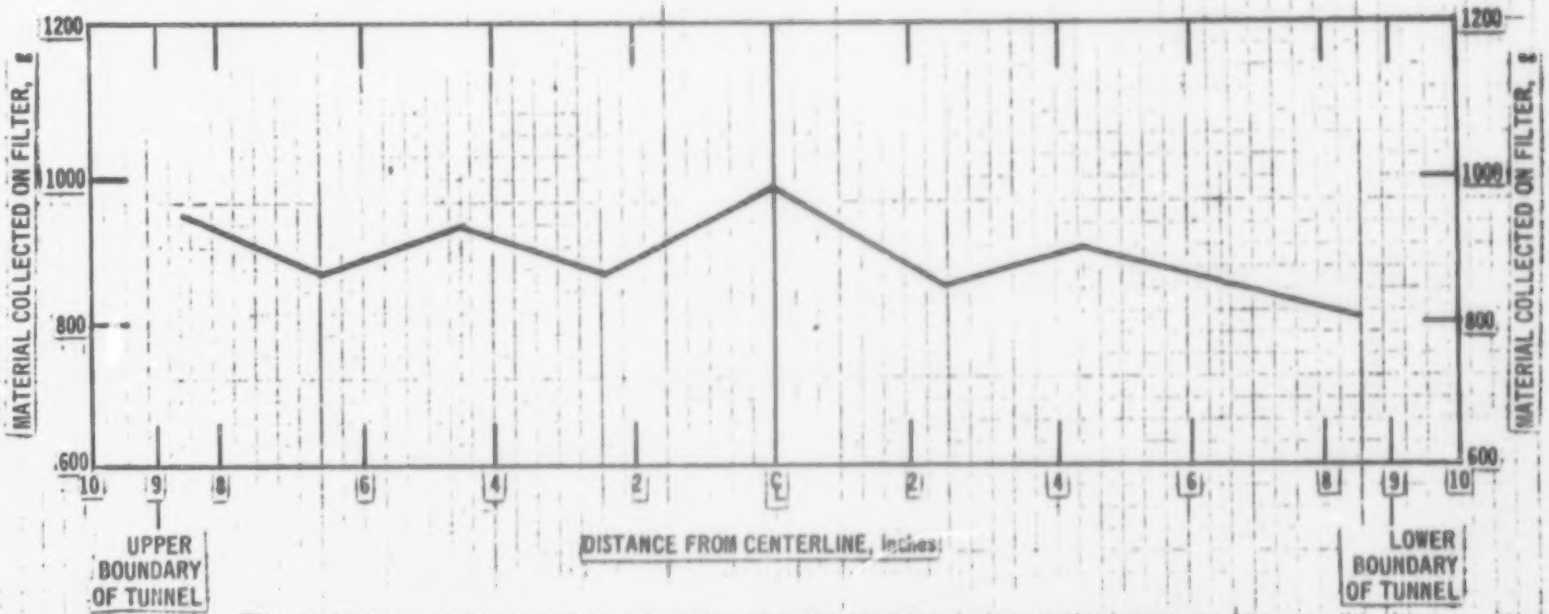


Fig 16. Filter weight plotted as a function of probe location during vertical traverse.

Particle deposition studies were performed on the 4 inch dilution tunnel, but not performed on the Y system, 18 inch tunnel because such studies had been previously conducted on an identical tunnel. In both cases the results were determined as follows:

1. The engine was operated over a specified number of cold start LA-4-S-3 cycles.
2. Particulate samples were taken and the total particulate emission was calculated.
3. The tunnels were washed with dichloromethane.
4. The wash was evaporated and the residue weighed.
5. Percent deposition was determined.

The results had indicated a 3 percent deposition of particulate in the 18 inch tunnel as compared with a 5.9 percent value in the 4 inch tunnel.

The 5.9 percent level in the 4 inch tunnel compares with a value of less than 1 percent found by Esso.(4) Since actual engine exhaust was used in the EPA study as opposed to the monodesperse aerosol (3.5 micron diameter) generated in the Esso study, the smaller, warmer exhaust particles were probably subjected more by the influence of thermophoretic forces resulting ultimately in a greater deposition upon the cold tunnel surfaces.

SECTION II

CONCLUSIONS

1. Reasonably good simulation of actual vehicular engine operation has been achieved in the case of the Y system engine-dynamometer set up.

2. The X system does not adequately simulate vehicular engine operation but it does yield repeatable results.

3. The 18 inch dilution tunnel is capable of representatively sampling particulate emissions from gasoline engines.

4. The emission of hydrocarbons, carbon monoxide, carbon dioxide, and nitrogen oxide can be accurately determined from both X and Y systems in accordance with the 1975 Federal Test Procedure.

SECTION II.

RECOMMENDATIONS

1. One of the reference test vehicles should be equipped with a drive shaft torque meter. This would enable the measurement and recording of instantaneous values of torque and engine rpm versus time, hence, accurate speed-load curves could be generated for comparison with those on the engine-dynamometer test stand.

2. In order to reasonably simulate vehicular engine operation, the X system engine-dynamometer set-up should be inertia compensated. A means should be implemented for inertially loading the engine such that speed-load curves correspond with those of the vehicular engine when driven over identical cycles.

3. The 4 inch diameter dilution tunnel should be operated on the Y system engine to compare particle collection data with the 18 inch tunnel. Such experiments would hopefully indicate the effects, if any, of sampling non-isokinetically.

4. Instrumentation should be installed to enable modal analysis of both gaseous and particulate emissions. A better understanding of the relationship between engine mode of operation and the resulting character of pollutant emissions is needed to better predict atmospheric quality as a consequence of emission control measures.

SECTION IV

REFERENCES

1. Environmental Protection Agency, Federal Register, Vol. 37, No. 175, Title 40, Part 85, Sept. 8, 1972.

2. J.B. Moran and O. J. Manary, Interim Report, PB196783, "Effect of Fuel Additives on the Chemical and Physical Characteristics of Particle Emissions in Automotive Exhaust", NAPCA, July, 1970.

3. K. Habibi, "Automotive Particulate Emissions and Their Control", SAE Paper 710638, October 24, 1970, Midland, Michigan.

4. M. Beltzer, R.J., Campion, and W.L. Petersen, "Measurement of Vehicle Particulate Emissions", SAE Paper 740286, Feb. 25 - Mar. 1, 1974, Detroit, Michigan.

5. EPA Contract EHS-70-101, The Dow Chemical Company, APTD-1567, March, 1973.

6. B. Dimitriades and D.E. Seizinger, "A Procedure for Routine Use in Chromatographic Analysis of Automotive Hydrocarbon Emissions", Environmental Science and Technology, Vol. 5, No. 3, p. 222, March, 1971.

7. T.G. Dzubay and R.K. Stevens, "Ambient Air Analysis with Dichotomous Sampler and X-Ray Fluorescence Spectrometer", Paper submitted to Environmental Science and Technology, May, 1974.

8. K. Klostermand and R.L. Bradow, "Direct Determination of Sulfur Dioxide from CVS -diluted AutomExhaust", NIEHS Symposiu, op.cit.

9. S. Tejada, "Determination of Soluble Sulfates in CVS Diluted Exhaust: An Automated Method", NIEHS Symposiu, op. cit.

APPENDIX A - Program Listings

Programs for reducing data are written using FOCAL-12 language on a PDP-12 computer. Two of the programs, one for reducing gaseous emission data from Y engine and the other for computing fuel economy on the X engine, are listed below.

1. Program to reduce gaseous emission data obtained during an EPA Urban Driving Schedule:

```
 L L,YENG1,1
*W
C FOCAL-12

01.02 A "TYPE IN DATA" A,B,C,D,E,E2,E3,AA,G,G2,G3
01.04 A U,U2,U3,P,Q,Q2,Q3,R,S,S2,S3,T
01.36 S N=-2
01.45 S VM=432*(1/60)*E*FSQT(543/AA)*(C-102)*528/760*AA
01.46 S H=43.478*A*B/(C-(B*A/100)); S V=1/(1-.0047*(H-75))
01.49 S W=(1-.01925*G-.000323*A)*U
01.51 S X=(1-.000323*A)*P
01.53 S Y=13.4/(G+(Q+W)*.0001)
01.55 S Z=G-R*(1-1/Y)
01.57 S BB=VM*Z*.00001633; S CC=S-T*(1-1/Y)
01.63 S DD=VM*.00005416*V*CC; S EE=W-X*(1-1/Y)
01.65 S ZZ=VM*.00003297*EE; S N=N+1
01.66 IF (N) 2.61,2.81,2.95

02.61 S H1=BB; S G1=DD;S R1=ZZ;S E=E2;S Q=Q2;S S=S2
02.62 S U=U2;S G=G2
02.66 T %,"VM",VM,!; T %,"DF",Y,!
02.73 G 01.49
02.81 S H2=BB;S G2=DD;S R2=ZZ;S E=E3;S G=G3;S U=U3
02.88 S Q=Q3;S S=S3
02.94 G 02.66
02.95 T %,"VM",VM,!;T %,"DF",Y,!

03.01 T %,"YHC",(.43*H1+H2+.57*BB)/7.5,!
03.02 T %,"YCO",(.43*R1+R2+.57*ZZ)/7.5,!
03.03 T %,"YNOX",(.43*G1+G2+.57*DD)/7.5
?03.28 @ 24.01
*
```

2. **Program to calculate fuel economy in miles per gallon:**

```
L L,XENG-E,1
*W
C FOCAL-12

01.02 A "TYPE IN ECON DATA" A,B,C,D,E,AA,G,U,P,Q,R,S,T,XX
01.45 S VM=(17.358333)*(E)*(.3283725)*(C-D)*528/760*AA
01.46 S H=43.478*A*B/(C-(B*A/100)); S V=1/(1-.0047*(H-75))
01.49 S W=(1-.01925*G-.000323*A)*U
01.51 S X=(1-.000323*A)*P
01.53 S Y=13.4/(G+(Q+W)*.0001)
01.55 S Z=Q-R*(1-1/Y)
01.57 S BB=VM*Z*.00001633; S CC=S-T*(1-1/Y)
01.63 S DD=VM*.00005416*V*CC; S EE=W-X*(1-1/Y)
01.64 S YY=(G-XX*(1-1/Y))*13000;S WW=YY*.00005185*VM
01.65 S ZZ=VM*.00003297*EE

02.61 S MM=BB/10.242;S NN=ZZ/10.242;S OO=WW/10.242
02.62 S QQ=DD/10.242
02.63 S PP=2423/((MM*.866)+(NN*.429)+(OO*.273))
02.65 T %,"HC-GPM",MM,!;T %,"CO-GPM",NN,!
02.66 T %,"VM",VM,!; T %,"DF",Y,!
02.67 T %,"NOX-GPM",QQ,!;T %,"MPG",PP,!
?03.24 0 16.37
*
```

The variables listed in both programs are identified as follows:

A = relative humidity, %
B = saturated vapor pressure of water, mm. of Hg.
C = barometric pressure, mm of Hg.
D = sample inlet pressure, mm of Hg.
E = time for bag 1, sec.
E2 = time for bag 2, sec.
E3 = time for bag 3, sec.
AA = temperature at inlet to venturi, °R
G,G2,G3 = concentration of CO_2 in bag 1, bag2, bag 3, respectively; ppm
U,U2,U3 = concentration of CO in bag 1, bag 2, bag 3, respectively, ppm
P = background concentration of CO, ppm
Q,Q2,Q3 = concentration of HC in bag 1, bag 2, bag 3, respectively, ppm
R = background concentration of HC, ppm.
S,S2,S3 - concentration of NO_x in bag 1, bag 2, bag 3, respectively, ppm
T = background concentration of NO_x, ppm
XX = background level of CO_2, %

Appendix B3.9

Status Report

ROAP 26AAE

Task 007

Protocol to Characterize Gaseous Emissions as a Function of Fuel and Additive Composition - Prototype Vehicles

This task was begun as a protocol development project at the Bureau of Mines. After completion of the basic program, it appeared that additional work was needed to respond to the non-regulated emissions milestones of January 1, 1975. Consequently, a new contract program was begun at Southwest Research Institute to determine fuel additive protocol test procedures for PNA, sulfur and nitrogen compounds, and such other species which may be of health effects interest as the in-house program proceeds. Future work will evaluate the control system performance protocol as well as performing tests on non-catalytic prototype engines.

Status:

Two water-brake dynamometers and control systems have been set up and 350 CID Chevy engines have been mounted and broken in. Test methods for active hydrocarbons, aldehydes, COS, H_2S, SO_2, SO_3, phosphine, PNA, nitrosamines, ammonia, and phenols have been set up and calibrated. Mileage accum-lation tests on the base fuel are in progress. Two other fuels, a high aromatics fuel, and the base fuel containing a full additive package trace levels of TEL and high sulfur will be run. It is anticipated that this program will be completed by late fall.

Appendix B3.10

Status Report
ROAP 26AAE
Task 009

Protocol to Characterize Particulate Emissions as a Function of Fuel and Additive Composition

Concept:

Again the concept associated with this task was to rely on a substantial contract effort at Dow to develop a standardized test method for particulate measurement. The rather small in-house effort was designed to validate Dow procedures and to extend sulfate characterization data to a variety of catalytic and non-catalytic prototype automobiles.

The Dow studies on Chevrolet vehicles and engines produced highly variable data. A statistical analysis of the Dow in-house particulate data is in progress in order to establish control levels for a draft protocol in progress.

The in-house work involved careful qualification testing of particulate sampling devices to establish their reliability with both sulfuric acid and organic aerosols. A paper on the EPA CVS-compatible system was presented at the NIEHS Symposium in April and a recent report on results with Exxon and EPA systems is included within Appendix B3. A report on non-catalyst and catalyst systems including determination of fuel sulfur level effects was prepared for submission as SAE paper 740528. Both monolithic and pelletted catalysts have now been studied in some detail.

Appendix B3.11

SOUTHWEST RESEARCH INSTITUTE
8500 CULEBRA ROAD • POST OFFICE DRAWER 28510 • SAN ANTONIO, TEXAS 78284

August 10, 1974

TO: Dr. Ronald Bradow, Project Officer
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

FROM: Charles T. Hare and Karl J. Springer
Department of Emissions Research
Southwest Research Institute
8500 Culebra Road
San Antonio, Texas 78284

SUBJECT: Interim Report on Phase I and Monthly Progress Report No. 13 for the period July 1 to July 31, 1974; Contract No. 68-02-1230, "Development of a Methodology for Determination of the Effects of Diesel Fuel and Fuel Additives on Particulate Emissions," SwRI Project No. 11-3718.

PREPARED FOR: Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Introduction

The purpose of this project is to develop and demonstrate a test procedure suitable for characterizing the effects of diesel fuels and fuel additives on particulate emissions from automotive (truck and bus) diesels. The scope of this work includes construction and use of a dilution tunnel for diesel exhaust, use of a variety of particulate sampling devices and techniques, and application of a wide range of chemical analyses to diesel particulate. This report covers the test protocol which has been developed to meet project objectives, including all assumptions and calculation techniques.

Conclusions and Final Results for Phase I

The Phase I effort, by agreement with the Project Officer, included: the development and construction of all necessary items of equipment; development of all necessary test and data reduction procedures; development of chemical analysis procedures for dimethylnitrosamine and phenols; and demonstration of the entire system protocol using one engine (Detroit Diesel

6L-71T) and one fuel (B, or emissions test No. 2 diesel). This scope of tasks under Phase I is that required under the contract except for the number fuels involved, but it was agreed that demonstration on one fuel would be sufficient to meet contract objectives.

A. Specification, Procurement, and Assembly of Equipment

The dilution tunnel itself was constructed of 3.18mm (1/8 inch) stainless steel sheet rolled into a tube of 273mm (17.7 in) inside diameter. It was made in two sections, each 2.44mm (8 ft) long, with flanged connections at the mid-point and at both ends. The tunnel is shown in Figure 1, along with: the dilution air cleanup filters (extreme left); the upper end of the high-volume sampling system (extreme right); the exhaust muffler and transfer pipe (below tunnel left of center); and the engine air intake system (vertical duct at left). The amount of exhaust flowing into the dilution tunnel is controlled in two ways. First, in addition to the small vertical transfer tube leading from the muffler to the tunnel, the muffler has two other (larger) outlets with gate valves to control flow through them. Closing the valves forces more sample into the dilution tunnel, and vice versa. As a second control parameter, the diameter of the perforated tube (inserted into the muffler) through which exhaust must pass to enter the (nominal) 3 inch O.D. transfer tube was varied to arrive at best maximum and minimum flowrates. The best diameter was found to be (nominal) 1 1/4 inch O.D. tubing. A sketch of the dilution tunnel is given as Appendix page A-2, including the internal details and critical dimensions.

Figure 2 is a detailed view of the adaptations made to the (nominal) 4-inch sampling system originally specified, including the tapered inlet (reduces cross-sectional area by about 33 percent) and the transition made to a (nominal) 8-inch by 10-inch high volume sampling system. This system originally had a 108mm (4.25 in) diameter inlet and used 102mm round filters. Flow through the high-volume system is set and measured by a calibrated orifice mounted in a "tailpipe" affixed to the blower exhaust.

The other sampling system used on the diluted tunnel flows is a set of four smaller units which are operated simultaneously. Figure 3 shows the portion of this system which is inside the tunnel when in operation, consisting of four probes mounted near the tunnel centerline. These probes have a nominal inside diameter of 12.7mm (0.5 inch) at the tip, and the stainless ducts are standard 1-inch O.D. tubing. A sketch of a probe is included as Appendix page A-3. In operation, the probe system is mounted as shown in Figure 4, with a 47mm stainless steel filter holder on each "arm". Flows through the four-probe system (or "4 x 47" system) are set and measured by the instruments shown in Figure 5. The four flowmeters are used to maintain isokinetic sample rates, and the total flow through

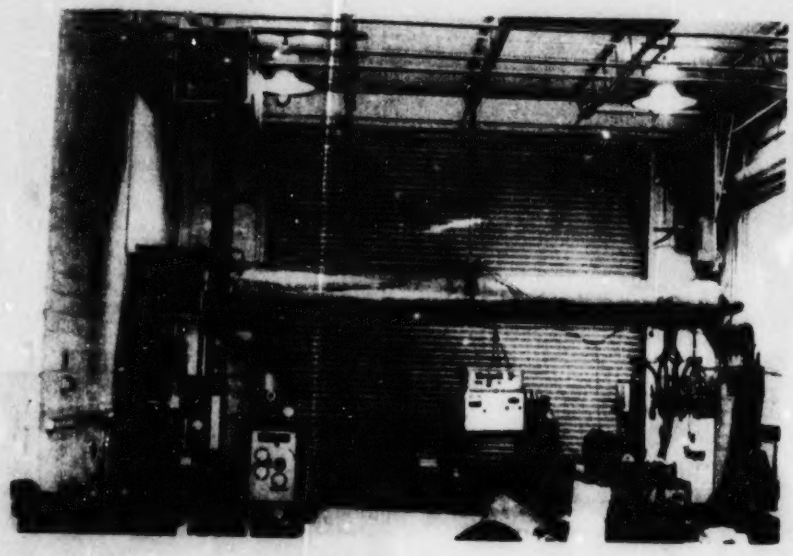


Figure 1. Diesel particulate dilution tunnel

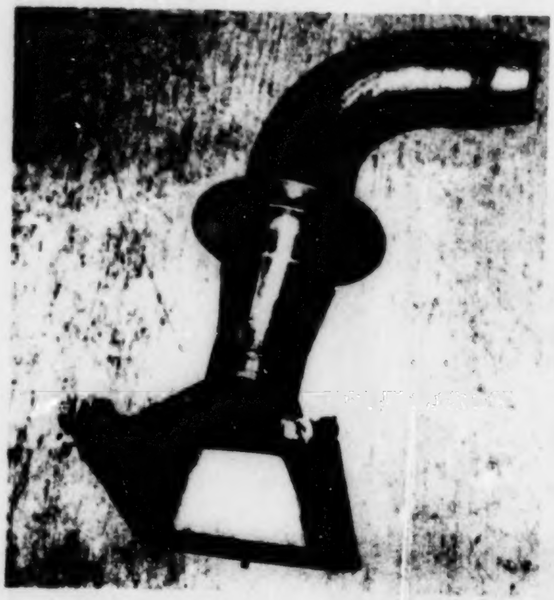


Figure 2. Modified 4-inch sampling system

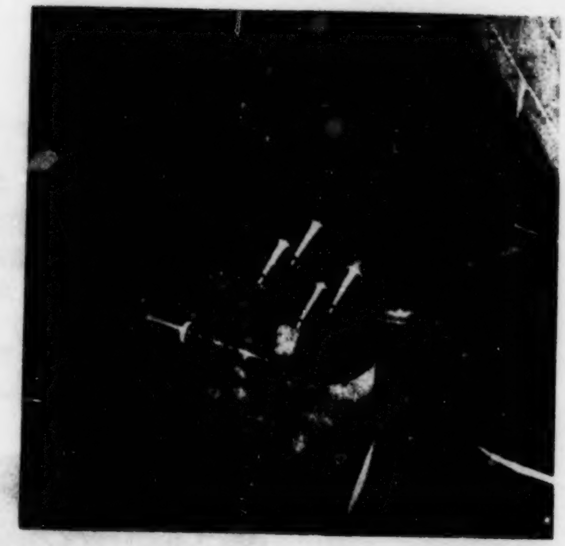


Figure 3. 4 x 47mm probe system

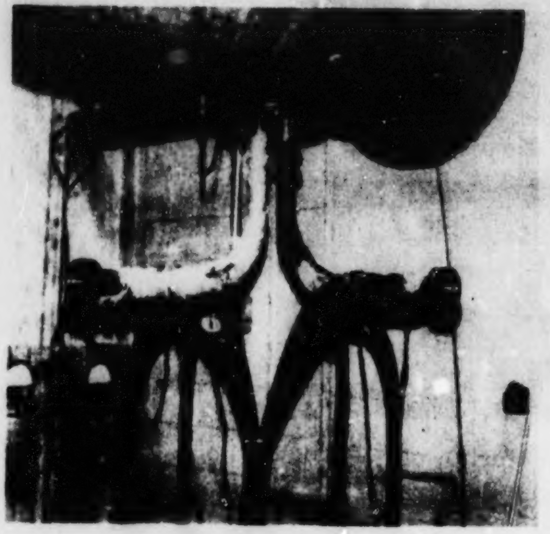


Figure 4. 4 x 47mm probe system mounted in tunnel

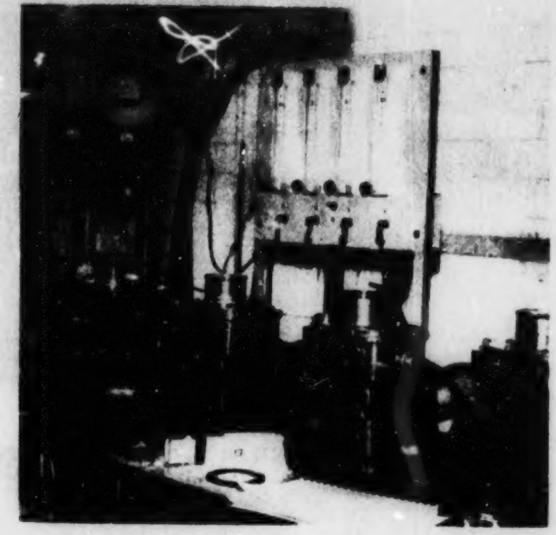


Figure 5. Flowmeters and dry gas meters used with 4 x 47mm sampling system

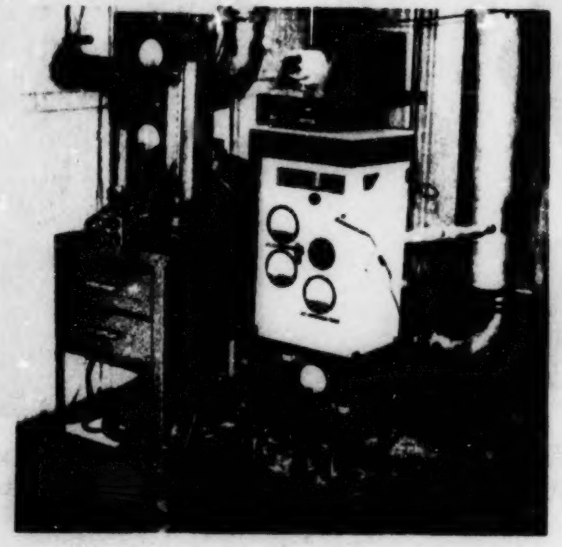


Figure 6. ERC sampler and peripheral equipment

each system for a given test is measured by one of the dry gas (totalizing) meters.

In addition to the tunnel techniques, particulate is collected during some runs by a diluter-sampler developed under a separate EPA contract. This "ERC sampler" is shown in Figure 6 (center), along with the sampling pumps, flowmeters, and dry gas meter (left) which are necessary to its operation. The particulate sample is actually collected in the 47mm filter holder below the ERC unit, and the exhaust sample for the ERC is extracted from the exhaust pipe just upstream of the muffler as shown in Figure 7 (connector in bend of elbow is probe insertion point). The sample probe used for the ERC unit has a tip inside diameter of 5.09mm (0.2005 in) and most of the fabricated sample line is (nominal) 1/2 inch O.D. stainless tubing. A sketch of the probe is included as Appendix page A-4. A section of (nominal)1/4 inch O.D. stainless tubing 152mm (6 in) long was inserted between the 1/2 inch line and the ERC (nominal) 5/8 inch diameter sample line to decrease sample flow somewhat.

Two other techniques are being used to evaluate particulate emissions from the engines under test, and they are both qualitative from the particulate mass standpoint. These techniques are the Federal (PHS) smokemeter, and the Bosch EFAW sampling/spot reading system. Figure 8 shows these techniques being applied back-to-back, with the Bosch sampling probe inserted into the pipe and the PHS optical unit in position on the end of the pipe. The PHS meter reads smoke plume opacity (remotely), and the Bosch system employs a reflective reading from a filter through which a standard volume of exhaust is drawn to place a value on smoke intensity. The PHS meter is the standard tool used to certify diesel engines in the United States for smoke performance, and the Bosch unit is widely used in engineering test and evaluation.

Up to this point, the engine used for testing and development work has been a Detroit Diesel-Allison 6L-71T unit, shown in Figure 9 as set up for operation in the test cell. The other engine to be used in the program is a Cummins NTC-290, to be tested after all six fuel configurations have been tried on the Detroit Diesel. A limited amount of testing has also been performed using two diesel-powered automobiles, an Opel and a Nissan. Figures 10 and 11 are two views of the experimental setup used for these light-duty vehicles, with a long exhaust pipe extension (insulated) to reach the dilution tunnel. Any regularly-scheduled test program on light-duty vehicles would probably utilize a tunnel mounted near the dynamometer rather than the existing tunnel, since the existing one is really intended only for bare engine usage.

The other major items of equipment needed for this test program are a microgram-sensitivity balance and a temperature- and humidity-controlled environment to house it. The system constructed for this

Figure 7. Direct exhaust sampling point for ERC sampler

Figure 8. Federal (PHS) smokemeter optical unit and sample acquisition for Bosch EFAW unit

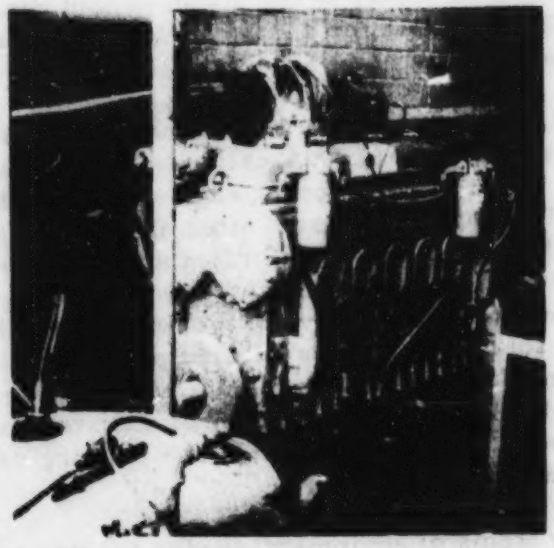


Figure 9. Detroit Diesel 6L-71T in test cell

Figure 10. Exhaust duct used for tests on Opel and Nissan diesel autos - first view

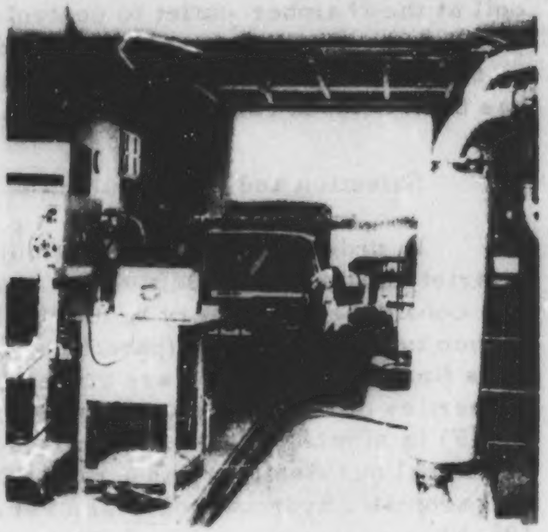


Figure 11. Exhaust duct used for tests on Opel and Nissan diesel autos - second view

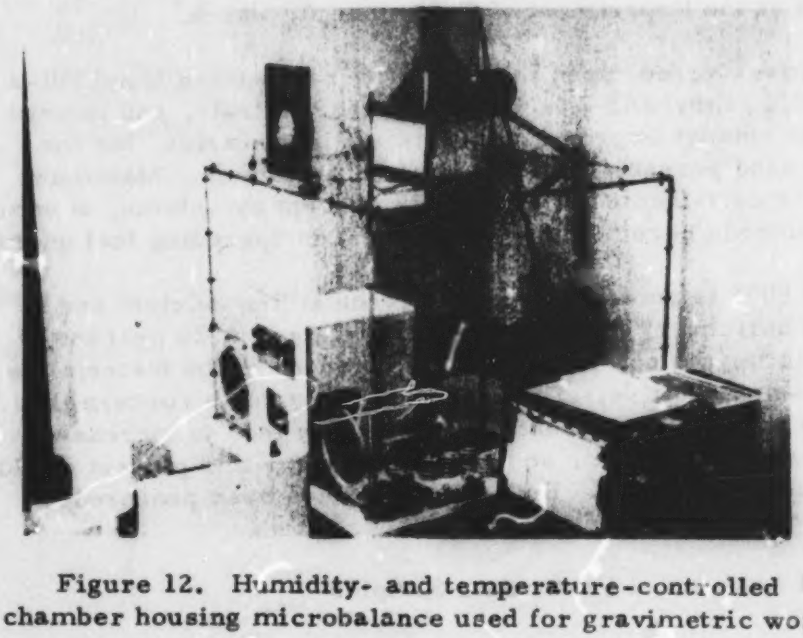


Figure 12. Humidity- and temperature-controlled chamber housing microbalance used for gravimetric work

project is shown in Figure 12, and it has yielded excellent results. The humidity control system consists of a large insulated spray chamber/ water tank/chilling unit through which all intake air is drawn, and a reheat coil at the chamber outlet to control temperature within ± 1°C. Absolute humidity has been observed to vary only slightly as the chilling unit cycles, on the order of 0.05% water vapor in the air. All air entering the chamber has been filtered twice by MSA Ultra-Aire systems, and the air is not recycled.

B. Selection and Procurement of Test Fuels and Additives

In order to fulfill contract objectives, it was desired to employ a variety of fuels and additives in evaluating the test protocol. Variation was considered necessary in fuel boiling range, sulfur content, and hydrocarbon type composition (paraffins, olefins, aromatics). The specifications finally agreed upon are given on page B-2 of the Appendix, and the properties of the fuels as received are given on page B-3. Fuel A (EM-197-F) is similar to a No. 1 kerosene fuel such as might be used in a municipal bus fleet. It has a rather low boiling range and density, about 10% aromatic hydrocarbons, and very low sulfur content. Fuel B (EM-195-F) is essentially a No. 2 diesel emissions test fuel, with a broad boiling range and about 35% aromatic hydrocarbons. This fuel has relatively high sulfur content and the highest density of the three test fuels. Fuel C (EM-198-F) falls between fuels A and B in density, fraction of aromatics, and sulfur content. The low end of its boiling range is truncated, however, because it is a specially-blended fuel and does not contain the normal range of base stocks. The three fuels were procured in amounts of at least 11,400 l (3000 gal) each and stored in specially-designated tanks at the Department of Emissions Research.

The additives agreed upon for use in the project are Ethyl DII-2 and Lubrizol 8005. Ethyl DII-2 is a primary hexyl nitrate, and is used as an ignition (or cetane) improver. Treatment level varies, but the most commonly used percentage is 0.1 percent by volume. Maximum treatment level is cost-limited at about 0.15 percent by volume, at which point refinery methods become more economical in upgrading fuel quality.

Lubrizol 8005 is an organo-metallic, containing calcium and a small amount of barium. The recommended dosage is 0.25 percent by volume, representing the optimum cost effectiveness of the material as a smoke-suppressing additive. There is apparently some concern that treatment levels above 0.25 percent by volume may lead to increased ash deposits over the long term, so the level used for this project would certainly not exceed that value. Both additives have been procured in amounts sufficient for project use.

C. Chemical Analysis of Particulate Samples

Several types of chemical analysis have been set up to process

samples of diesel particulate taken during this project. To begin, a commercial laboratory has been retained to perform quantitative S, C, H, and N analysis on samples deposited on 47mm glass fiber filters, as well as S, C, H, N, and O analysis on organic solubles. It is currently planned to submit 56 samples per engine for S, C, H, and N analysis, and 20 samples of solubles per engine for S, C, H, N, and O analysis. The total test/analysis matrix will be described later in the report, showing exactly which modes and fuels will be analyzed.

Another commercial laboratory will be performing trace metal analysis on samples collected on 47mm Fluoropore filters (0.5μm mean flow pore size). The metals to be analyzed for are summarized in Table 1, along with nominal detection limits in μg/cm^2 filtration area and μg/filter based on a nominal effective filtration area of 13 cm^2. Calcium and Zinc were included in the test array at the last moment because a trial sample showed them to be significant. The current test plan calls for submittal of 96 samples for trace metal analysis, which should yield a good picture of variation in particulate metal content with fuel and additive composition.

Analysis of particulate samples for total soluble organic content is being performed by a research group at Southwest Foundation, the Institute's sister organization which deals mostly with basic medical research. The solubles are extracted in chloroform, and subsequent analysis for BaP is performed by thin-layer chromatography. Spectral analysis of the soluble fraction is performed by NMR and IR, and the remaining sample is split for SCHNO analysis and paraffin determination.

TABLE 1. METALS TO BE ANALYZED AND
NOMINAL DETECTION LIMITS

	Nominal Detection Limit	
Element	μg/cm^2	μg/filter*
Ba	0.24	3.1
Ca	0.12	1.6
Mn	0.10	1.3
Pb	0.14	1.8
Sn	0.26	3.4
Ni	0.10	1.3
Cu	0.10	1.3
V	0.12	1.6
Sr	0.14	1.8
Zn	not known	not known

* based on effective filtration area of 13cm^2

Copies of NMR and IR spectra run on early practice samples are included as Appendix C for information purposes.

Paraffins will be separated from total organic solubles by liquid chromatograph, and a boiling point distribution will be obtained by FID using ASTM D 2887-72T or a similar technique. This analysis will be performed on a work order basis by the U.S. Army Fuels and Lubricants Research Laboratory, which is located on the Institute grounds and staffed by Institute personnel.

The SwRI Department of Chemistry and Chemical Engineering has been working under this contract to develop analysis methods for nitrosamines, phenols, and organic peroxides in diesel particulate. The procedures for nitrosamines (n-dimethylnitrosamine in particular) seem to be working well on test samples, and the phenol technique appears to have adequate sensitivity. The rectangular glass fiber filters used to collect samples have a variable and sometimes quite significant phenol background level, however, and filter washing has been only partially successful in eliminating the problem. A new type of highly "cleaned-up" filter is currently coming on the market, and we should receive our first batch in a few weeks. It is hoped that this development will yield significantly better results. Tests designed to yield samples for phenol analysis are being skipped in the current test schedule, and these specific runs will be made later after the problems have been ironed out.

Efforts were made to find an approach to analysis for organic peroxides, but no real success was achieved. The level of effort allocated for development of analytical methods and actual tests did not permit a very broad-ranging development effort, and it was decided that the attempt for peroxides should be dropped to avoid jeopardizing the number of actual evaluations needed for phenols and nitrosamines. A summary of the methods developed for phenols and DMNA is given in Appendix D along with some early sample chromatograms.

D. Development of Test Plan and Data Matrix

Since the total number of samples being taken for this project is extremely large, a test plan was devised to meet project objectives while avoiding unnecessary duplication. The information gathered from the tests conducted should be ample to decide which types of analysis lend themselves most readily to fuel and additive qualification. The test plan and data matrix are summarized in Table 2. Following this plan (with no extra runs) yields the following numbers of independent analytical determinations on each engine:

1. 312 gravimetric (other than ERC)
2. 48 trace metals

TABLE 2. TEST PLAN AND DATA MATRIX FOR EACH ENGINE

	Operating Condition		Analysis Codes* by Sampling System		
			4 x 47	Hi-Vol	
Fuel(s)	Speed	Load, %		First Run	Rpt.
B	Idle	---	1 2 5 8	1 3 4 6	1 7
	Peak Torque	0	1 2 5 8	1	
	Peak Torque	25	1 5 8	1	
	Peak Torque	50	1 2 5 8	1 3 4 6	1 7
	Peak Torque	75	1 5 8	1	
	Peak Torque	100	1 2 5 8	1	
	Rated	0	1 2 5 8	1	
	Rated	25	1 5 8	1	
	Rated	50	1 2 5 8	1	
	Rated	75	1 5 8	1	
	Rated	100	1 2 5 8	1 3 4 6	1 7
	Composite		1 2 5 8	1 3 4 6	1 7
B + 8005	Idle	---	1 2 5 8	1 3 4 6	1 7
	Peak Torque	0	1 2 5 8	1	
	Peak Torque	25	1 5	1	
	Peak Torque	50	1 2 5 8	1 3 4 6	1 7
	Peak Torque	75	1 5	1	
	Peak Torque	100	1 2 5 8	1	
	Rated	0	1 2 5 8	1	
	Rated	25	1 5	1	
	Rated	50	1 2 5 8	1	
	Rated	75	1 5	1	
	Rated	100	1 2 5 8	1 3 4 6	1 7
	Composite		1 2 5 8	1 3 4 6	1 7

* Analysis Codes

1. Gravimetric
2. Trace Metals
3. Organic Solubles, BaP, IR, NMR
4. Paraffins
5. SCHN (Particulate)
6. SCHNO (Organic Solubles)
7. Phenols and Nitrosamines
8. ERC Gravimetric

TABLE 2 (Cont'd). TEST PLAN AND DATA MATRIX FOR EACH ENGINE

			Analysis Codes* by Sampling System		
	Operating Condition		4 x 47	Hi-Vol	
Fuel(s)	Speed	Load, %		First Run	Rpt.
A and C	Idle	---	1 2 5 8	1 3 4 6	1 7
	Peak Torque	0	1 2 5 8	1	
	Peak Torque	25	1 8	1	
	Peak Torque	50	1 2 5 8	1 3 4 6	1 7
	Peak Torque	75	1 8	1	
	Peak Torque	100	1 2 5 8	1	
	Rated	0	1 2 5 8	1	
	Rated	25	1 8	1	
	Rated	50	1 2 5 8	1	
	Rated	75	1 8	1	
	Rated	100	1 2 5 8	1	
	Composite		1 2 5 8	1 3 4 6	1 7
A + DII-2 and C + 8005	Idle	---	1 2 5 8	1 3 4 6	1 7
	Peak Torque	0	1 2 5 8	1	
	Peak Torque	25	1	1	
	Peak Torque	50	1 2 5 8	1	
	Peak Torque	75	1	1	
	Peak Torque	100	1 2 5 8	1	
	Rated	0	1 2 5 8	1	
	Rated	25	1	1	
	Rated	50	1 2 5 8	1	
	Rated	75	1	1	
	Rated	100	1 2 5 8	1 3 4 6	1 7
	Composite		1 2 5 8	1 3 4 6	1 7

* Analysis Codes

1. Gravimetric
2. Trace Metals
3. Organic Solubles, BaP, IR, NMR
4. Paraffins
5. SCHN (Particulate)
6. SCHNO (Organic Solubles)
7. Phenols and Nitrosamines
8. ERC Gravimetric

3. 20 organic solubles, BaP, IR, NMR, paraffins and SCHNO on the organic solubles, phenols, and nitrosamines
4. 56 SCHN on particulate
5. 60 ERC gravimetric.

A certain number of additional runs will have to be made, of course, to allow for data errors, instrument failures, and so forth.

E. Gaseous Emissions, Smoke Opacity, and Bosch Smoke Numbers for One Engine and One Fuel

To document the emissions of the 6L-71T engine, tests have been conducted for both smoke and gaseous emissions. These tests were intended to make certain that the engine is typical of its model and to provide baseline smoke and gaseous emissions data on Fuel B (the fuel specified in the Federal Register for diesel gaseous emissions and smoke test purposes). The 13-mode steady-state smoke data by Bosch sampling and PHS meter are shown in Table 3, and these data indicate low smoke levels at all conditions. An additional set of full-load runs was made in 200 rpm increments from 2100 rpm to 1100 rpm; and the average PHS smoke opacities were: 1.2 percent at 2100 rpm, 1.0 percent at 1900, 1.0 percent at 1700, 2.0 percent at 1500, 4.0 percent at 1300, and 11.8 percent at 1100 rpm.

Gaseous emissions were also run on the 13-mode procedure, and the cycle composite results are shown in Table 4. The computer tabulations of the gaseous emissions results are given as Pages E-2 through E-4 of Appendix E. These emissions agree well with certification data on similar engines, so the major operational variables of the engine seem to be in order. Transient smoke results were obtained using the Federal Smoke Test Procedure and PHS smokemeter, and the transcribed data sheets appear as Pages E-5 through E-7 of the Appendix. A summary of these data is given in Table 5. Similar tests for gaseous emissions and smoke will be performed using the other 5 fuels as permitted by the overall test schedule.

F. Dilution Tunnel Calibration

The blower used to pull dilution air and exhaust through the dilution tunnel system was calibrated using a large laminar flow element and some electric heaters, and the result is shown on page F-2 of Appendix F, with supporting data and calculations on pages F-3 and F-4. It was necessary to extrapolate the line back to a blower Δp of 3.5 inches H_2O because the measurement system precluded readings with a Δp under 12 inches H_2O. The higher blower speed is being used to permit higher tunnel velocities and consequent higher ample acquisition rates. The calibration with the 36:26 drive and 3.5 inches H_2O blower Δp yields tunnel bulk velocity down-

TABLE 3. STEADY-STATE BASELINE SMOKE DATA FOR 6L-71T ENGINE ON FUEL "B" (EM-195-F)

			PHS % Opacity by Run			Bosch Filter Reflectance Data by Run							
Mode	RPM	Load	2	3	4	1A	1B	2A	2B	3A	3B	4A	4B
1	480	----	0.1	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.2	0.2
2	1600	----	0.2	0.3	0.3	0.1	0.1	0.2	0.2	0.1	0.1	0.2	0.2
3	1600	25%	0.5	0.5	0.6	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
4	1600	50%	0.6	0.7	0.7	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
5	1600	75%	0.8	0.9	0.9	0.6	0.6	0.6	0.6	0.4	0.4	0.8	0.8
6	1600	100%	1.3	1.7	1.8	1.0	1.0	0.5	0.5	1.0	1.0	1.4	1.4
7	480	----	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
8	2100	100%	1.0	1.0	1.0	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
9	2100	75%	0.8	0.9	0.8	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.4
10	2100	50%	0.6	0.8	0.7	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.4
11	2100	25%	0.6	0.7	0.7	0.2	0.2	0.3	0.3	0.2	0.2	0.2	0.2
12	2100	----	1.0	0.7	0.8	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.5
13	480	----	0.1	0.3	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.2

TABLE 4. SUMMARY OF 13-MODE CYCLE COMPOSITE GASEOUS EMISSIONS FOR 6L-71T ENGINE ON FUEL "B" (EM-195-F)

	Cycle Composite Emissions, g/hp-hr			
Run	HC	CO	NO_x	HC + NO_x
1-1	0.49	2.66	11.6	12.1
2-1	0.44	2.33	11.7	12.2
2-2	0.58	2.10	12.6	13.1
Avg.	0.50	2.36	12.0	12.5

TABLE 5. FEDERAL SMOKE TEST DATA FOR 6L-71T ENGINE, FUEL "B"

	Percent Opacity by PHS Smokemeter		
Run	"a" Factor	"b" Factor	"c" Factor
1	11.9	1.4	20.6
2	12.8	2.1	20.8
3	13.0	1.9	21.8
Avg.	12.6	1.8	21.1

stream of the sampling point

$$V_b = (11.9)\,\frac{\text{blower revolutions (counts)}}{\text{time, sec}}\;\frac{T_s}{T_B} \times \frac{P_B}{P_s}$$

where the "S" station is the sample acquisition point and the "B" station is the blower inlet. The constant in the equation for V_{sb} (bulk velocity at the sampling point) is 11.9 for the 4 x 47 system and 12.4 for the hi-vol system due to greater sample withdrawal rate).

Velocity profiles at the sampling station were acquired with a Thermo Systems hot-film anemometer. The results were less precise than anticipated, due to the influence of large-scale turbulence in the duct. Averages over a number of runs gave usable values, however, and the plots shown on Appendix page F-5 were constructed from these data (included as Appendix F-6 through F-8). The positions as well as the velocities in these profiles are referred to the duct centerline, and although the "flat" sections of the profiles are not quite normal to the axis, the deviation from centerline velocity ($V_{℄}$) is only about ± 2% in the sampling zone. The reason for the higher velocities in the upper right section of the tunnel is probably the overhead lighting which strikes the tunnel from that direction. The tunnel can be insulated, or the lights can be shaded if the profile distortion is felt to be a problem, but the ± 2% velocity gradient in the sampling zone is probably much less a cause of anisokentic sampling than the large scale turbulence mentioned earlier.

Temperature and concentration profiles were also taken (vertical only), and the results are shown on pages F-9 and F-10 of Appendix F. They are essentially flat so no comment is required.

G. Calibration of Sampling Systems and Engine Airflow Instrumentation

Measurement of flow through the hi-vol sampling system (the one which uses (nominal, 8 x 10 inch glass fiber filters) is performed by noting the pressure drop through an orifice mounted about 0.79m (31 in) downstream of the sampling blower outlet in a 76mm (3 in) O.D. tube "tailpipe".

Temperature is also measured at the orifice, so mass flow can be calculated by the formula

$$\text{mass flow} = 5.35 \left(\frac{\Delta p\, p_a}{T}\right)^{0.5} \text{lbm/min} = 2.43 \left(\frac{\Delta p\, p_a}{T}\right)^{0.5} \text{kg/min}$$

where p_a is the atmospheric pressure in inches of Hg. The constant (5.35) was determined by calculation using the ASME flowmeter handbook procedure.

Flowrate measurements for the four-probe system using 47mm filters are taken via flowmeters, and the calibration curves for the specific meters employed are shown on page G-2 of Appendix G. Calculations and data on which the flowmeter curves are based are given as pages G-4 through G-6 of Appendix G. These latter four pages also contain data and calculations used to arrive at correction factors for readings of the dry gas meters used to indicate total flow through each 47mm filter during the sampling period. Flowmeter number 5 is used on the ERC sampler, and it was calibrated in the same way as numbers 1 - 4. The calibration curve for flowmeter 5 is included as page G-7.

The orifice used to measure engine air flow was calibrated against a laminar flow element which has a calibration traceable to NBS standards. The final equation (derived by applying the best squares method to the logs of Δp and mass flow) is

$$\dot{M}_a = 89.60 \left(\Delta p \rho\right)^{0.4842} \text{lbm/min} = 40.64 \left(\Delta p \rho\right)^{0.4842} \text{kg/min},$$

and its derivation is given on pages G-8 through G-11 of Appendix G. Exhaust mass flow is simply air flow plus (directly measured) fuel flow.

H. Development of Simplified Operating Criteria for ERC Sampler and Dilution Tunnel

After the ERC sampler was cleaned and made operable by a number of minor corrections and repairs, it was decided that the instructions supplied with it were not suitable for use by technical staff in the laboratory. There is some question, as a matter of fact, that the operating procedure as given in the instructions is workable at all. It was decided, therefore, to review the sampler's principles of operation and devise a more usable set of operating instructions. The instructions themselves appear as pages H-2 through H-8 of Appendix H, and they are lucid enough for our technicians to follow with only a little help. The calculations and considerations leading to the instructions are presented as pages H-9 through H-16 of Appendix H, and some simplified operating guides for the dilution tunnel itself are given as pages H-17 and H-18.

I. Development of Mode Weighting Procedure for 13-Mode Tests

Obtaining a sample on one filter which is a true composite for the 13-mode test requires that the total amount of raw exhaust gas filtered in each mode be proportional to the product of engine exhaust mass flowrate and the time-based weighting factor for that mode. In mathematical terms

$$m_i = C_1 \left(\frac{E+D}{E}\right)_i W_i (\dot{M}_e)_i \quad \text{or} \quad (M_{or})_i = C_2 \left(\frac{E+D}{E}\right)_i W_i (\dot{M}_e)_i ,$$

where:
i = individual mode, $i = 1, 2, 3, \ldots, 13$;
$m_i = (\dot{m}_i)\,(\text{time})_i$ = total dilute exhaust filtered in mode i, 4 x 47 system, lb_m;
$(M_{or})_i = (\dot{M}_{or})_i\,(\text{time})_i$ = total dilute exhaust filtered in mode i, hi-vol system, lb_m;
$(\text{time})_i$, = time in mode i, sec;
$(\dot{M}_e)_i$ = engine exhaust flowrate in mode i, lb_m/min;
W_i = time-based weighting factor;
E_i = exhaust flow through tunnel, lb_m/min; and
D_i = diluent flow through tunnel, lb_m/min.

Note that

$$(\text{time})_i = \frac{C_1}{\dot{m}_i}\left(\frac{E+D}{E}\right)_i W_i(\dot{M}_e)_i = \frac{C_2}{(\dot{M}_{or})_i}\left(\frac{E+D}{E}\right)_i W_i(\dot{M}_e)_i ,$$

so $$C_1 = C_2 \frac{\dot{m}_i}{(\dot{M}_{or})_i}$$

Therefore, since both $\dot{m}_i$ and $(\dot{M}_{or})_i$ are essentially fixed by isokinetic considerations, it is sufficient to use only one of the $(\text{time})_i$ equations above for computation purposes. The quantities $\left(\frac{E+D}{E}\right)_i$, W_i, $(\dot{M}_e)_i$, and $(\dot{M}_{or})_i$ are known or can be calculated from experimental data. If a value for any $(\text{time})_i$ is assumed, the constant C_2 can be calculated and then the other $(\text{time})_i$ can also be calculated. To determine whether or not our choice of C_2 is reasonable, we can compute

$$(\text{time}) = \sum (\text{time})_i ,$$

and choose a higher or lower value of C_2 to make (time) more reasonable.

To minimize the complexity of the 13-mode test, it was decided to determine the $(E+D/E)_i$ with both the dump valves open (minimum exhaust backpressure). This decision means that we will not have the absolute maximum particulate collection per unit time, but the latest experimental data show that an adequate amount should be collected in a test of about 40 minutes' duration. It was also possible, of course, to determine $(\dot{M}_e)_i$ and a good average value for $\dot{M}_{or}$ while measuring the dilution ratios. The data and some calculations are given in Table 6

TABLE 6. DATA AND CALCULATIONS USED TO DETERMINE MODE WEIGHTS

i= Mode	W_i	$\left(\frac{E+D}{E}\right)_i$	$(\dot{M}_e)_i$	Time in Mode (min) by Assumption	
				1	2
1	0.20/3	32.2	9.85	2.00	1.08
2	0.08	22.6	35.78	6.12	3.31
3	0.08	19.8	37.63	5.64	3.05
4	0.08	20.4	41.64	6.43	3.48
5	0.08	19.4	46.73	6.86	3.71
6	0.08	18.1	54.14	7.42	4.01
7	0.20/3	31.5	9.85	1.96	1.06
8	0.08	12.9	74.43	7.27	3.93
9	0.08	14.4	67.45	7.35	3.97
10	0.08	15.8	60.36	7.22	3.90
11	0.08	16.3	54.16	6.68	3.61
12	0.08	17.6	50.79	6.76	3.66
13	0.20/3	27.1	9.85	1.68	0.91
			TOTAL = (time) =	73.39	39.68

ASSUMPTION 1: $(\text{time})_1 = 2.00$ min $\therefore C_2 = 0.1665$
conclusion: (time) too long $\therefore$ assume smaller C_2

ASSUMPTION 2: $C_2 = 0.09$
conclusion: (time) OK, but combine 1, 7, and 13 to make one longer idle mode so technicians will have adequate time to gather data

and on the lines just below Table 6, and the final schedule for the "11-mode" runs is given in Table 7 (an "11-mode" is just a "13-mode" with the 3 idle modes combined as mode 6). This schedule yields the desired result, that is, weighting of modes so as to make a single filter representative of a 13-mode test as that test is defined. If too small an amount of particulate is collected during the test as scheduled, it can be repeated.

J. Procedures for Data Reduction

Preparations discussed thus far have dealt with acquisition of good samples by correct methods, analysis of samples to determine their composition, and the number of samples which should be taken to ensure that an engine's entire range of particulate output is represented. This section gives the final technical developments necessary to calculate engine total

TABLE 7. WEIGHTING SCHEDULE FOR "11-MODE" COMPOSITE RUNS

Mode = i	Condition		Mode Time, Sec	Cumulative Time, sec
	Rpm	Load, %		
1	Peak Torque	0	198	198
2	" "	25	183	381
3	" "	50	208	589
4	" "	75	222	811
5	" "	100	240	1051
6	Idle	-	182	1233
7	Rated	100	235	1468
8	"	75	238	1706
9	"	50	234	1940
10	"	25	216	2156
11	"	0	219	2375

particulate output (and consequently the output of any species for which analysis is conducted) from data obtained during the course of a test. Data which are acquired during testing are perhaps best shown by the data forms which are filled out by the people running the tests, so the three types of forms are included as pages I-2 through I-4 of Appendix I. For a given test, only half of each data form would be completed (either top or bottom).

Mathematical development of data reduction procedures is given as pages I-5 and I-6 of Appendix I, largely based on the results of calibrations discussed in section G and calculations discussed in section H. Although the calculations are compact enough to be performed by hand for a few cases, the large number of samples being taken for this project make computer processing more economical in the long term. Examples of the encoding sheets from which data will be keypunched (12 data cards per test) are given as pages I-7 and I-8. The computer program being used for the processing is included as pages I-9 through I-12, and sample results are given on pages I-13 and I-14.

Possible Problems and Corrective Action

The only problem in view at this time is the continuing background interference with the Phenol analysis, and it is hoped that the new "clean" filters currently on order will eliminate the difficulty.

Plans for the Next Reporting Period

It is planned that all samples on fuels A, B, and C for the Detroit Diesel engine, except possibly those for Phenol analysis, will have been acquired. It is also planned that chemical analysis of all samples taken

while using fuels B and C will be complete or well underway. The gravimetric calculations (using the computer) should be well underway by the end of the next reporting period.

Submitted by:

Charles T. Hare

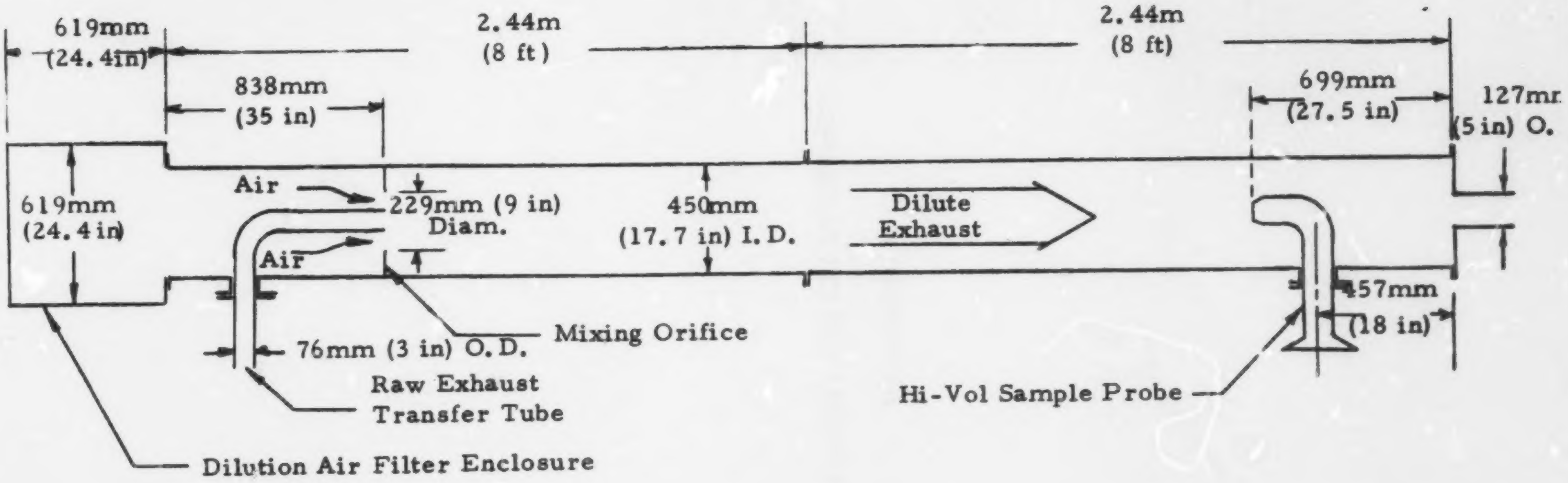
Charles T. Hare
Manager, Advanced Technology
Department of Emissions Research

Karl J. Springer

Karl J. Springer
Director
Department of Emissions Research

APPENDIX A

EQUIPMENT DESIGN SKETCHES

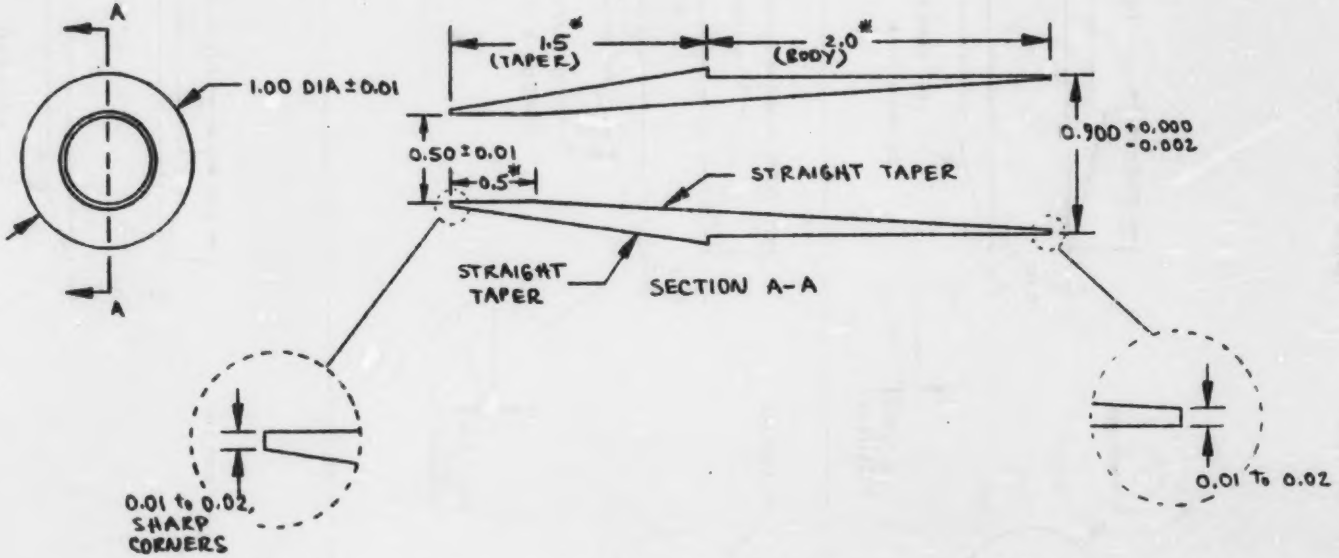

619mm
(24.4in)
2.44m
(8 ft)
2.44m
(8 ft)
838mm
(35 in)
699mm
(27.5 in)
127mr
(5 in) O.
Air
Air
619mm
(24.4 in)
229mm (9 in)
Diam.
450mm
(17.7 in) I.D.
Dilute
Exhaust
457mm
(18 in)
76mm (3 in) O.D.
Mixing Orifice
Raw Exhaust
Transfer Tube
Hi-Vol Sample Probe
Dilution Air Filter Enclosure

SCHEMATIC SECTION OF DILUTION TUNNEL FOR DIESEL PARTICULATE SAMPLING

SAMPLING NOZZLE
MAKE 4 EACH FROM
STAINLESS STEEL
11-3718-001 HARE 2646

DIMENSIONS IN INCHES

INSIDE STRAIGHT SECTION (TIP) DIAMETER SHOULD BE 0.50 ± 0.01, FINAL DIAMETER TO BE READ TO 3 SIGNIFICANT FIGURES AND MARKED ON OUTSIDE OF NOZZLE BODY (STRAIGHT SECTION)


A
A
1.00 DIA ± 0.01
1.5* (TAPER)
2.0* (BODY)
0.50 ± 0.01
0.5*
0.900 +0.000 -0.002
STRAIGHT TAPER
STRAIGHT TAPER
SECTION A-A
0.01 to 0.02, SHARP CORNERS
0.01 To 0.02

* THESE DIMENSIONS NOT CRITICAL:
OUTSIDE TAPER 1.5 To 2.0 LENGTH
OUTSIDE BODY 1.5 To 2.0 LENGTH
INSIDE STRAIGHT SECTION LENGTH 0.5 To 1.0
USE STANDARD TAPERS WHERE POSSIBLE

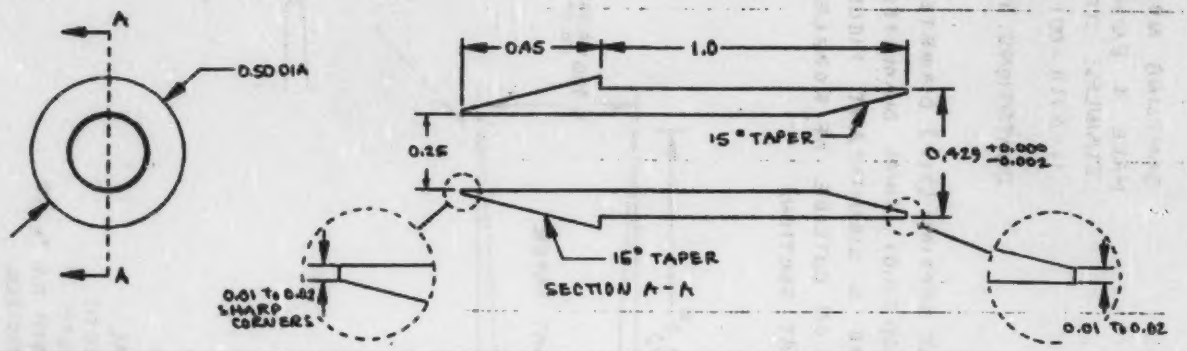
CHARGE 11-5718-001
DIMENSIONS IN INCHES
NOT TO SCALE

TOLERANCES ARE
± 0.01 UNLESS
NOTED OTHERWISE

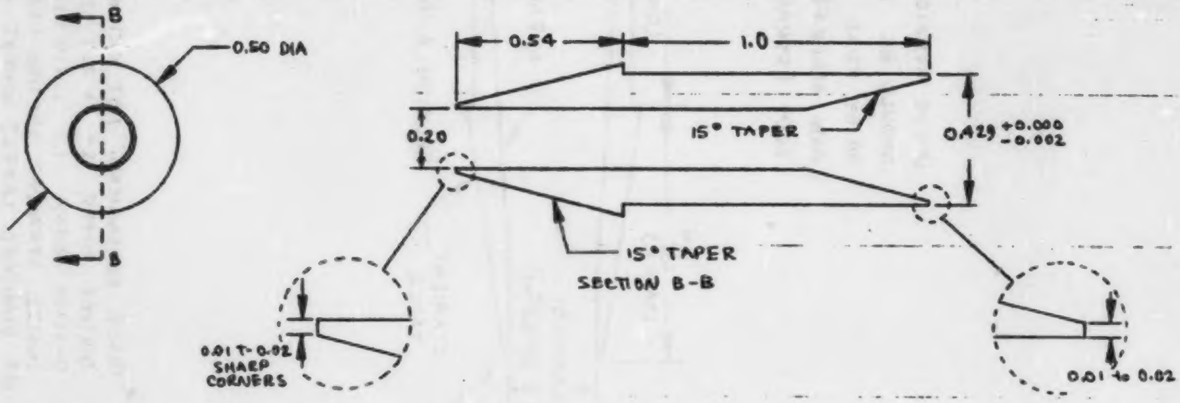
MATERIAL: STAINLESS STEEL
MAKE 1 EACH
HARE — 2646

MEASURED ID'S: #2; 0.2535
#3; 0.2005
#4; 0.3036

NOZZLE #2

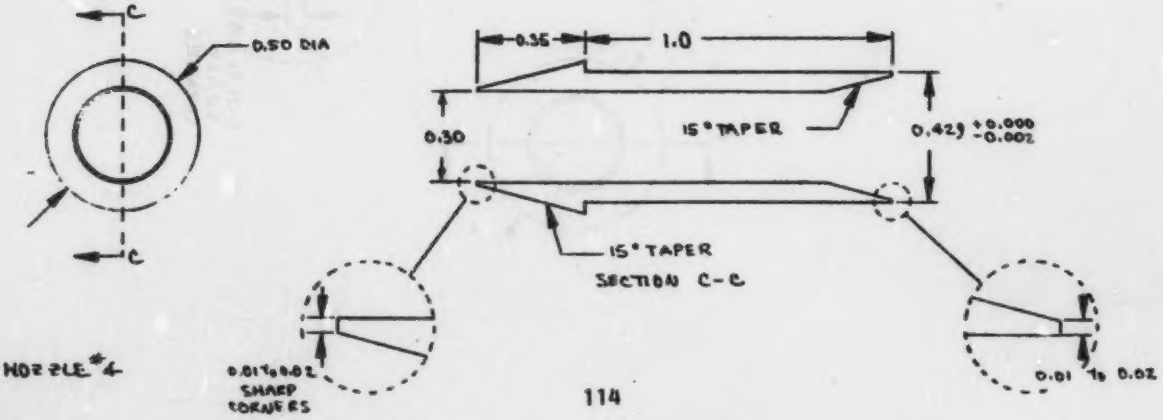


A
0.50 DIA
A
0.45
1.0
15° TAPER
0.25
0.429 +0.000 −0.002
15° TAPER
SECTION A-A
0.01 To 0.02 SHARP CORNERS
0.01 To 0.02



B
0.50 DIA
B
0.54
1.0
15° TAPER
0.20
0.429 +0.000 −0.002
15° TAPER
SECTION B-B
0.01 T- 0.02 SHARP CORNERS
0.01 to 0.02

NOZZLE #3



C
0.50 DIA
C
0.35
1.0
15° TAPER
0.30
0.429 +0.000 −0.002
15° TAPER
SECTION C-C
0.01 to 0.02 SHARP CORNERS
0.01 to 0.02

NOZZLE #4

APPENDIX B

FUEL SPECIFICATIONS AND INSPECTION

DIESEL FUEL SPECIFICATIONS
SWRI PROJECT 11-3718-001

	Emissions Test Type 2-D		Test Fuel A			Test Fuel C	
	Max	Min	Max	Min	Blend 1	Desired	Blend 10-11-73
FIA Analysis							
Aromatics, %		27(1)	10	5	8	20	20
Olefins, %			2	-	1	1	1
Saturates, %		Remainder	95	88	91	79	79
Distillation							
IBP, °F	400	340	310	240	320	about 370	432
10%, °F	460	400	340	320	331	430-440	449
50%, °F	540	470	400	380	379	480±20	463
90%, °F	610	550	480	440	456	550 max	508
EP, °F	660	580	500	480	492	580	580
Sulfur, %	0.5	0.2(2)	0.05	-	.007	0.05 max	
Nitrogen, %			0.02	-			
Cetane	50	42	60	48	46	40 min	47.5
Gravity, °API	37	33	55	50	47.4	40	38.7
Flash Point, °F		130		120			
Viscosity, cs	3.2	2.0		1.5		2 min	

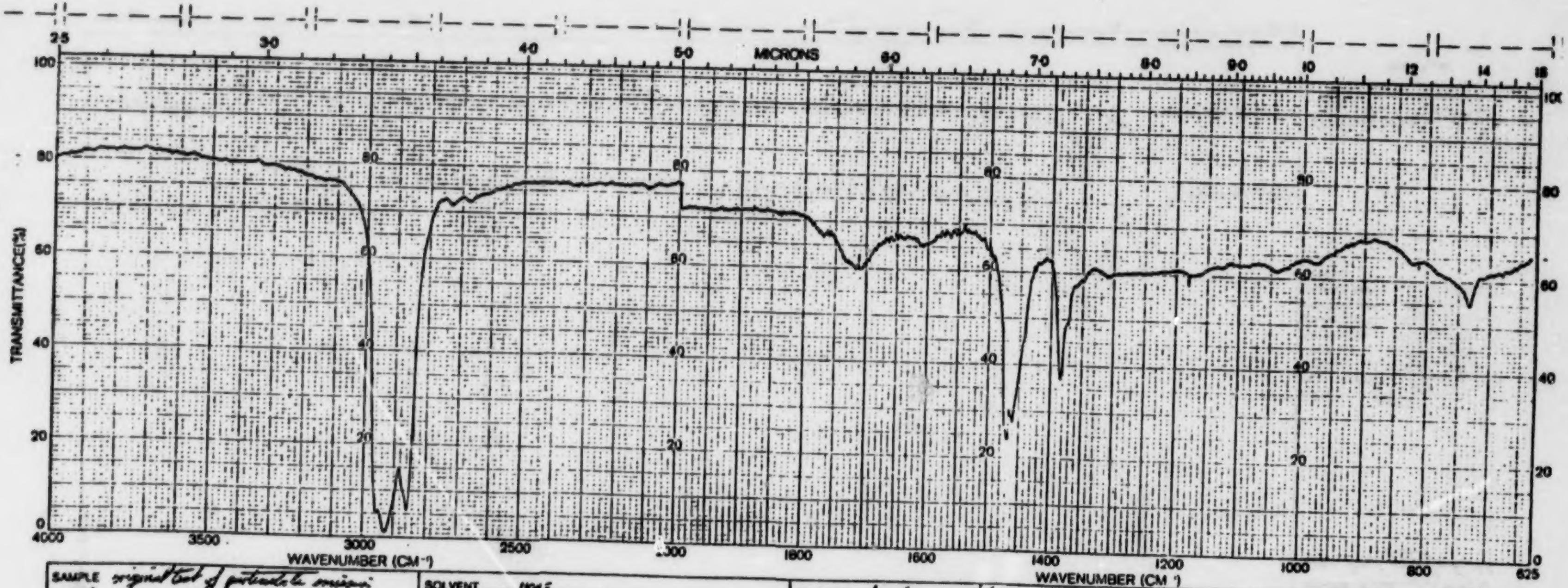
(1) Must not exceed 35 percent for Project 11-3718-001
(2) Should be around 0.3 percent for Project 11-3718-001

ANALYSIS OF FUELS TO BE USED DURING DIESEL PARTICULATE MEASUREMENT PROJECT

Project Fuel Cose	A	B	C
SwRI Fuel Code	EM-197-F	EM-195-F	EM-198-F
Fuel Type	No. 1 Kerosene	2D Emissions	"No. 1-1/2"
Distillation, °F			
IBP	330	384	410
10%	354	434	426
20%	360	460	441
30%	366	483	446
40%	376	500	450
50%	387	518	455
60%	402	531	460
70%	418	548	465
80%	437	569	479
90%	460	601	502
EP%	525	673	594
% Recovery	99	98	99
% Residue	1	2	1
% Loss	0	0	0
Aromatics, %	9.2	35.1	23.0
Olefins, %	0.8	0.0	1.0
Saturates, %	90.0	64.9	76.0
Gravity, °API	46.8	34.9	39.4
Cetane (Calculated)	51.0	49.5	49.5
Total Sulfur, %	0.003	0.319	0.010
Weight % C	85.0	86.5	85.3
Weight % H	13.9	12.8	13.9
Weight % N	0.08	0.10	0.04
Viscosity, cs	1.62	2.7	2.12
Flash Point, °F	130	176	185+

APPENDIX C

SAMPLE NMR AND IR SPECTRA RUN ON EARLY ORGANIC SOLUBLES SAMPLES



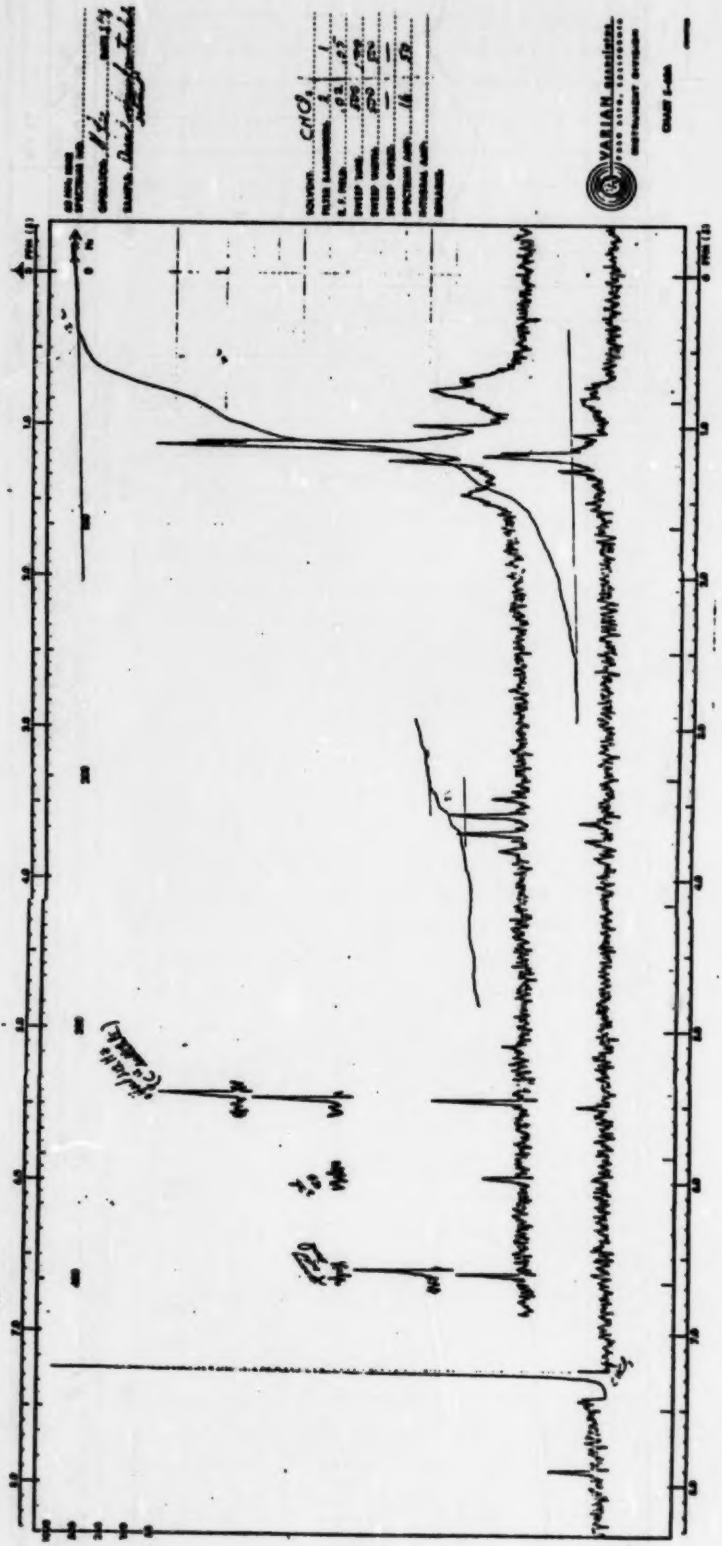
SAMPLE original test of particulate emission
test
ORIGIN

SOLVENT none
CONCENTRATION neat
CELL PATH —
REFERENCE

REMARKS Sample evaporated on a KBr crystal from a CHCl₃ solution

SCAN SPEED Medium
SLIT N
PERKIN ELMER
PART NO. 472-5099

OPERATOR [illegible]
DATE 3/14/74
REF. No.


CHCl3
VARIAN associates

APPENDIX D

PROCEDURES AND EARLY SAMPLE DATA FOR PHENOL AND NITROSAMINE ANALYSIS

Method for Determination of Phenols and N-Dimethylnitrosamine in Particulate Matter Collected on Glass Fiber Filter

1. Cut filter in pieces approximately 5 x 40 mm and place in 200-ml round bottom distillation flask.
2. Add 70 ml of 1% H_3PO_4 in water.
3. Connect distillation flask to vertically mounted small diameter (8 mm O.D.) water cooled condensing tube. This distillation set-up is similar to a Kjeldahl distillation apparatus.
4. Place 5 ml of 50% KOH in 50 ml beaker and place beaker so that outlet end of condenser tube is immersed in KOH solution.
5. Distill over 35 ml H_2O and rinse condenser tube with 5 ml H_2O. Should now be approximately 45 ml in beaker.
6. Transfer, without rinsing, contents of beaker to 125-ml separatory funnel.
7. Add 13 gm NaCl to funnel and shake to dissolve.
8. Rinse condenser tube with 10 ml benzene and collect in 50 ml beaker.
9. Transfer benzene to separatory funnel containing distillate and shake vigorously for 1 minute.
10. Drain aqueous phase into another 125-ml separatory funnel. Discard benzene.
11. Add 10 ml dichloromethane (DCM) to separatory funnel containing aqueous phase and shake vigorously for 1 minute.
12. Collect DCM in small vial and save.

13. Add 10-ml hexane to separatory funnel and shake well.

14. Drain aqueous phase into 100-ml volumetric flask. Discard hexane.

15. Add 1 drop Phenolphthale in Indicator Solution to aqueous phase.

16. Add concentrated H_3PO_4 to aqueous phase to indicator endpoint then add 2-3 drops excess H_3PO_4.

17. Cool to room temperature and add 0.5 ml diisopropyl ether (DIE).

18. Shake vigorously for 1 minute and immediately pour into 50-ml volumetric flask using appropriate funnel.

19. Swirl contents of stoppered flask and then allow DIE to collect on aqueous surface in neck of flask.

20. Insert ground glass stopper, to which has been attached a short length (60 mm) of 2-mm I.D. capillary tubing, into mating glass joint on flask.

21. Using a syringe and needle, inject water into flask through previously inserted silicone plug in flask body, so as to force the DIE up into the capillary tube.

22. Using a micro syringe, withdraw 5µl of DIE and inject into gas chromatograph for analysis of phenols.

23. The DCM previously saved is transfered to a micro concentrator and evaporated down to 0.5-0.75 ml.

24. 20µl of the concentrate DCM extract is injected into a gas chromatograph equipped with an Electrolytic Conductivity Detector used in the pyrolitic mode for selective detection of N-nitrosamines.

CHROMATOGRAPHIC CONDITIONS

Phenols

Column: 6' 10% OV-3 + 1% FFAP on 80-100 mesh Gas-Chrom Q-AWDMS

Column Temp: 125°C

Detector: FID

Detector Lens: 16X

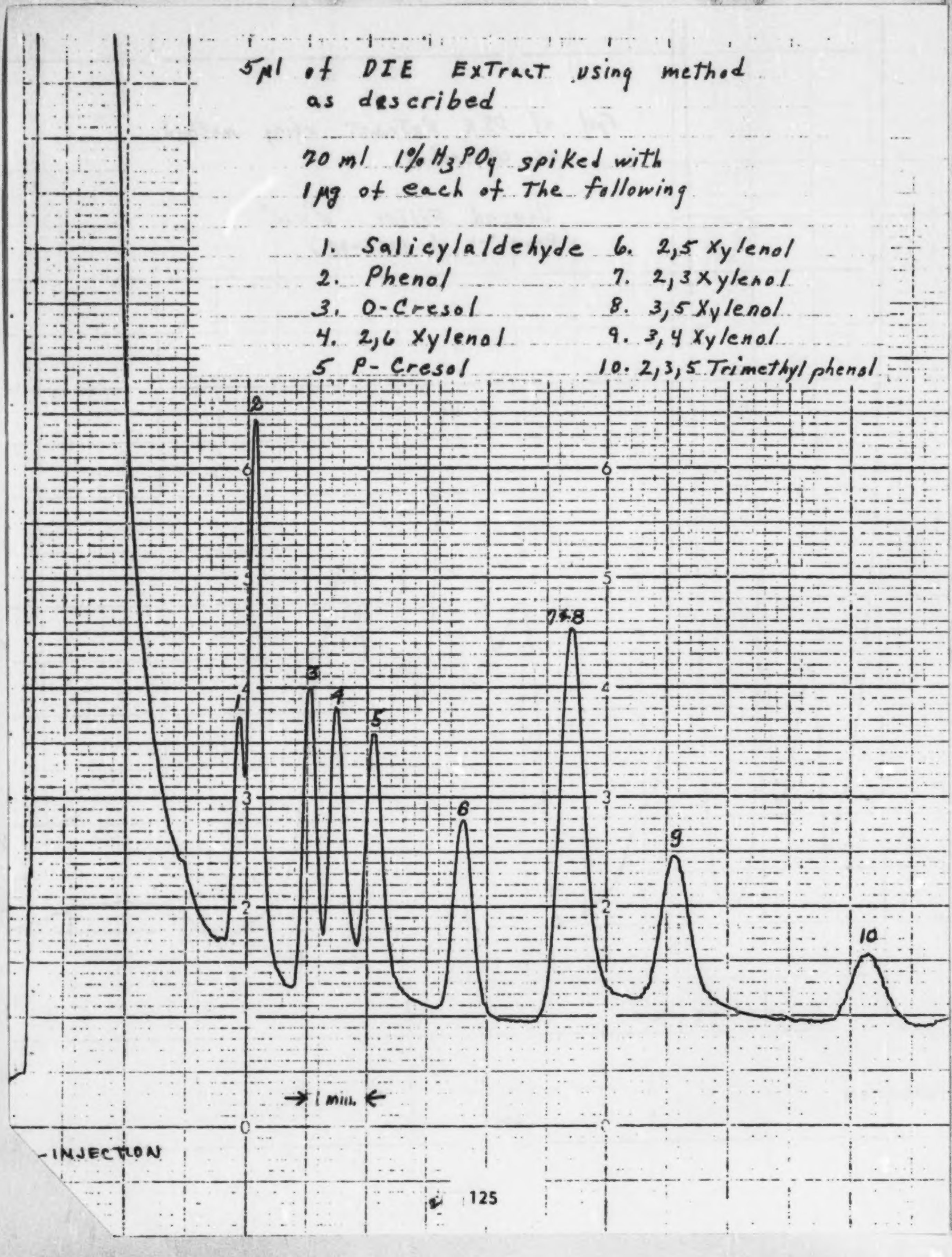
Dimethylnitrosamine

Column: 6' 10% Carbowax 1540 + 10% KOH on 60-80 Gas-Chrom Q

Column Temp: 125°C

Detector: Electrolytic Conductivity (Pyrolytic mode)

Detector Lens: 1X



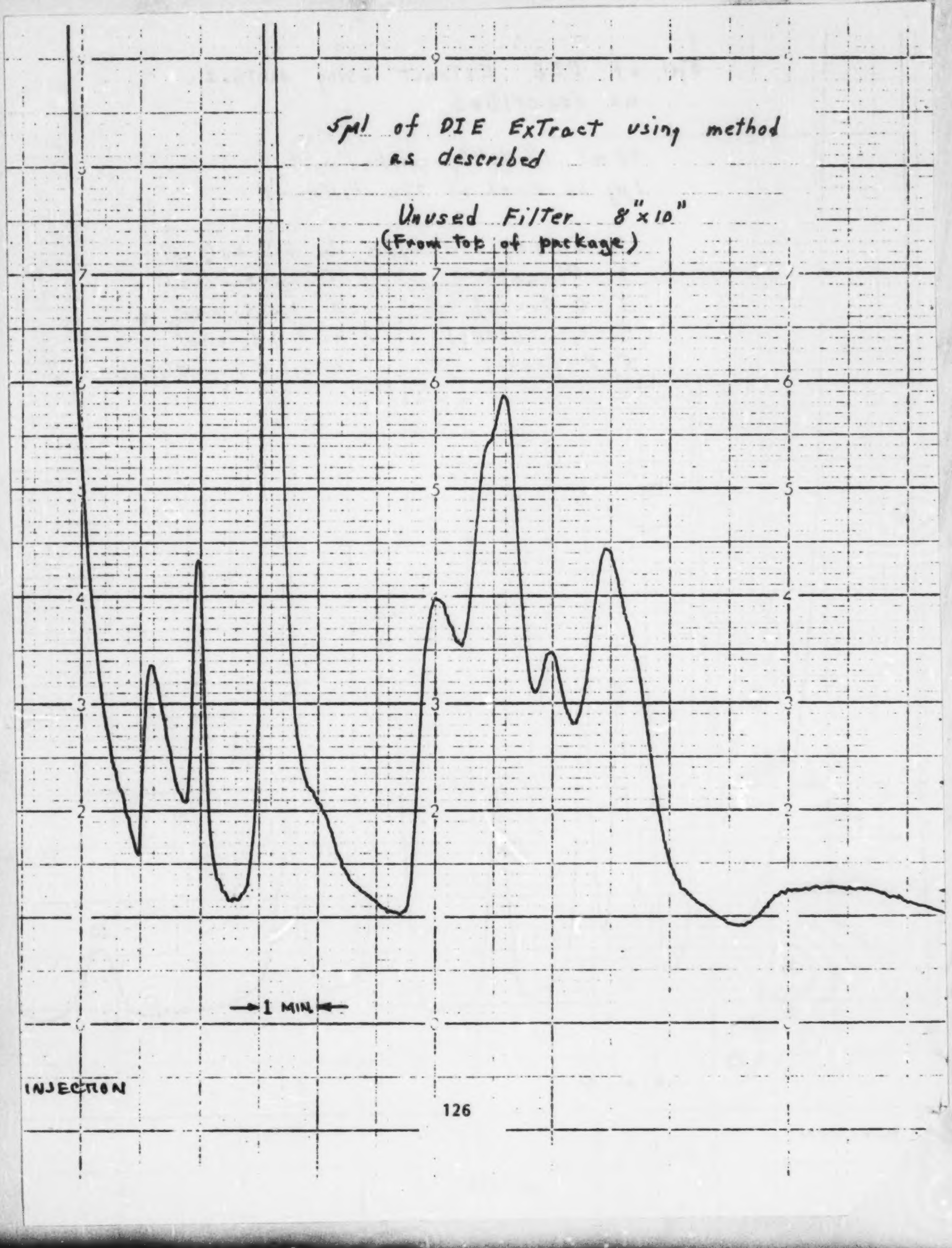
5 µl of DIE Extract using method as described

70 ml 1% H_3PO_4 spiked with 1 µg of each of the following

1. Salicylaldehyde
2. Phenol
3. O-Cresol
4. 2,6 Xylenol
5. P-Cresol
6. 2,5 Xylenol
7. 2,3 Xylenol
8. 3,5 Xylenol
9. 3,4 Xylenol
10. 2,3,5 Trimethyl phenol

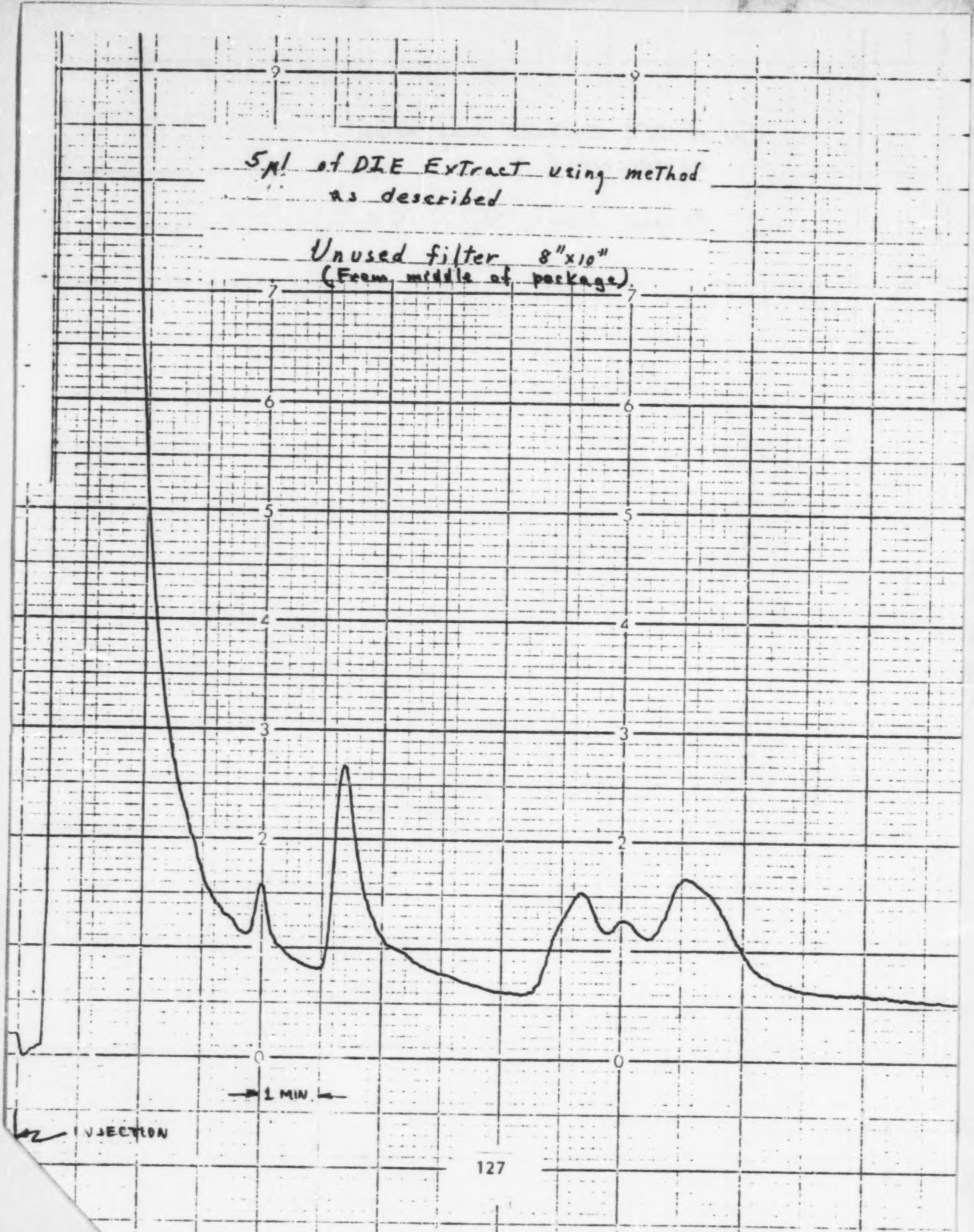
→ 1 min. ←

-INJECTION



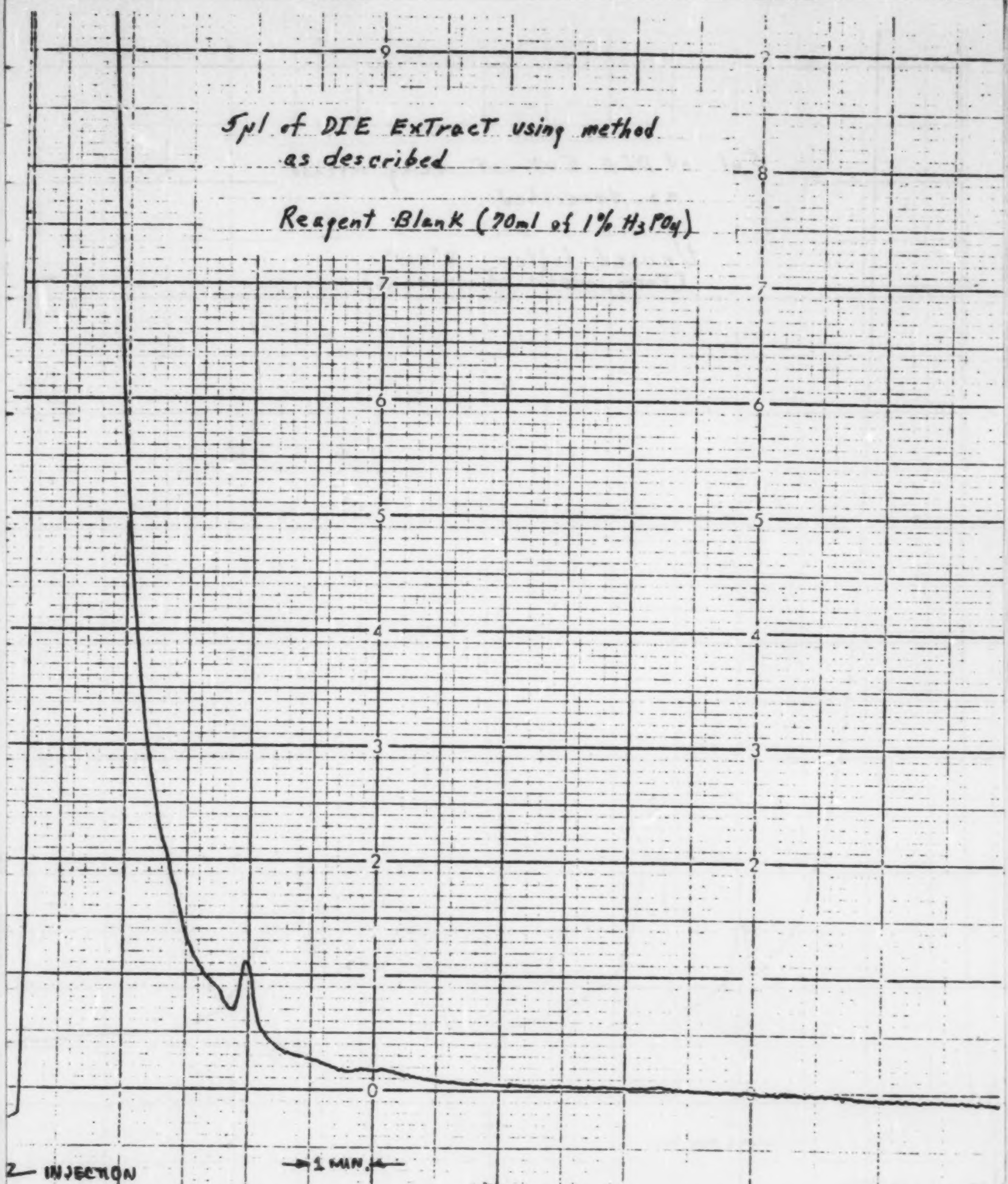
5µl of DIE Extract using method as described

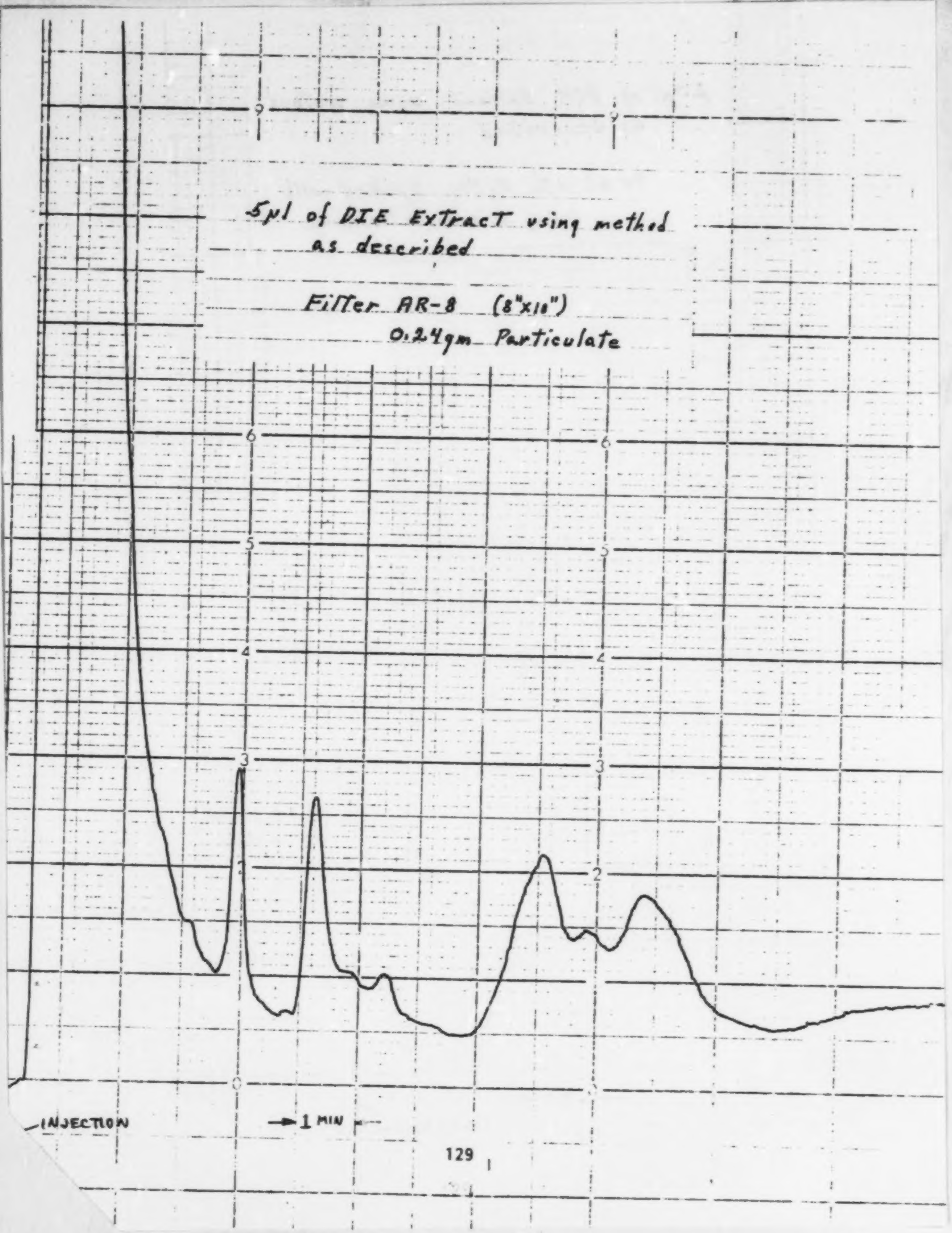
Unused Filter 8"x10"
(From top of package)



5µl of DIE Extract using method as described

Unused filter 8"x10"
(From middle of package)


5µl of DIE ExTracT using method as described
Reagent Blank (70ml of 1% H_3PO_4)
9
8
7
6
5
4
3
2
0
INJECTION
1 MIN.

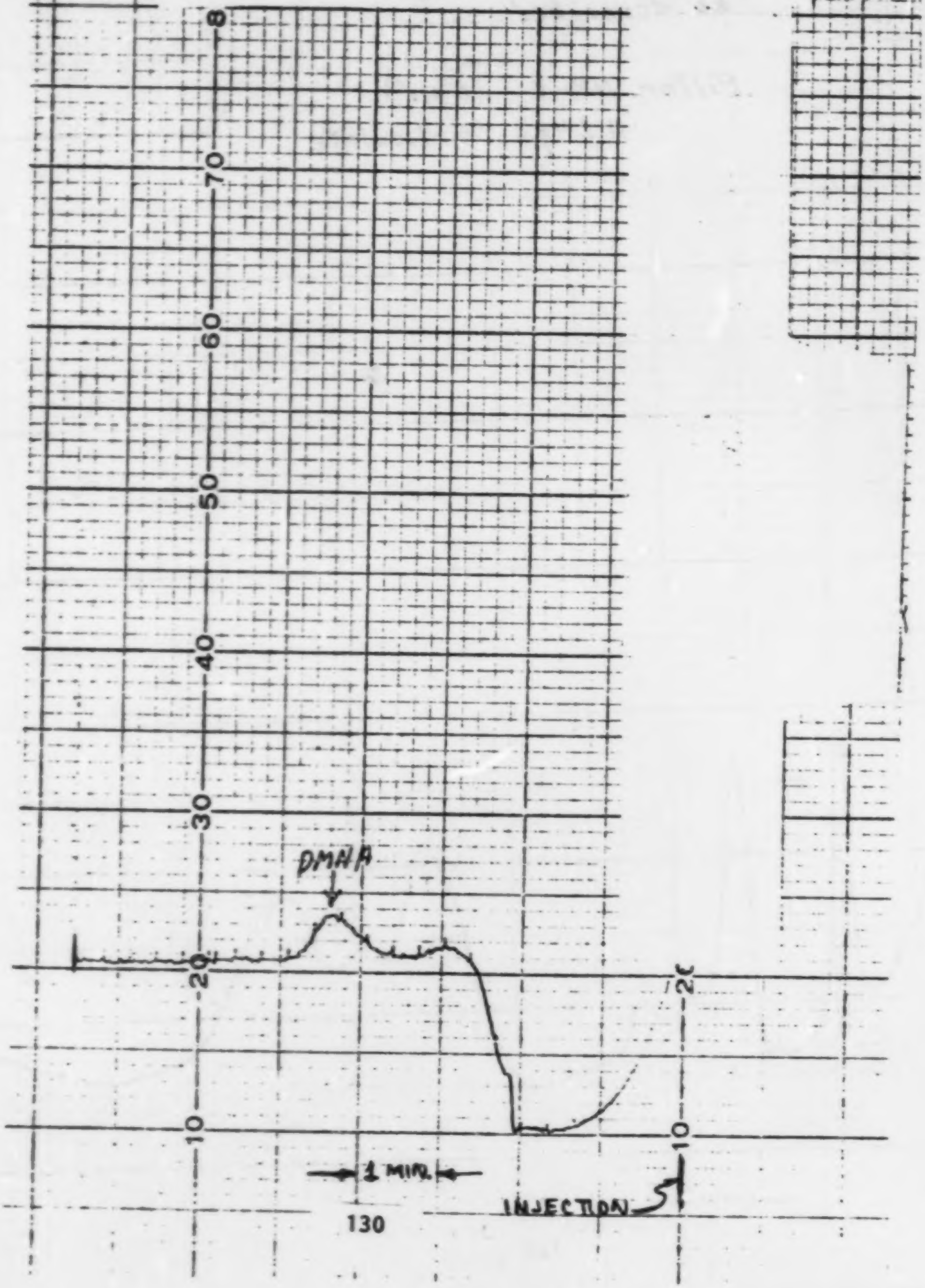


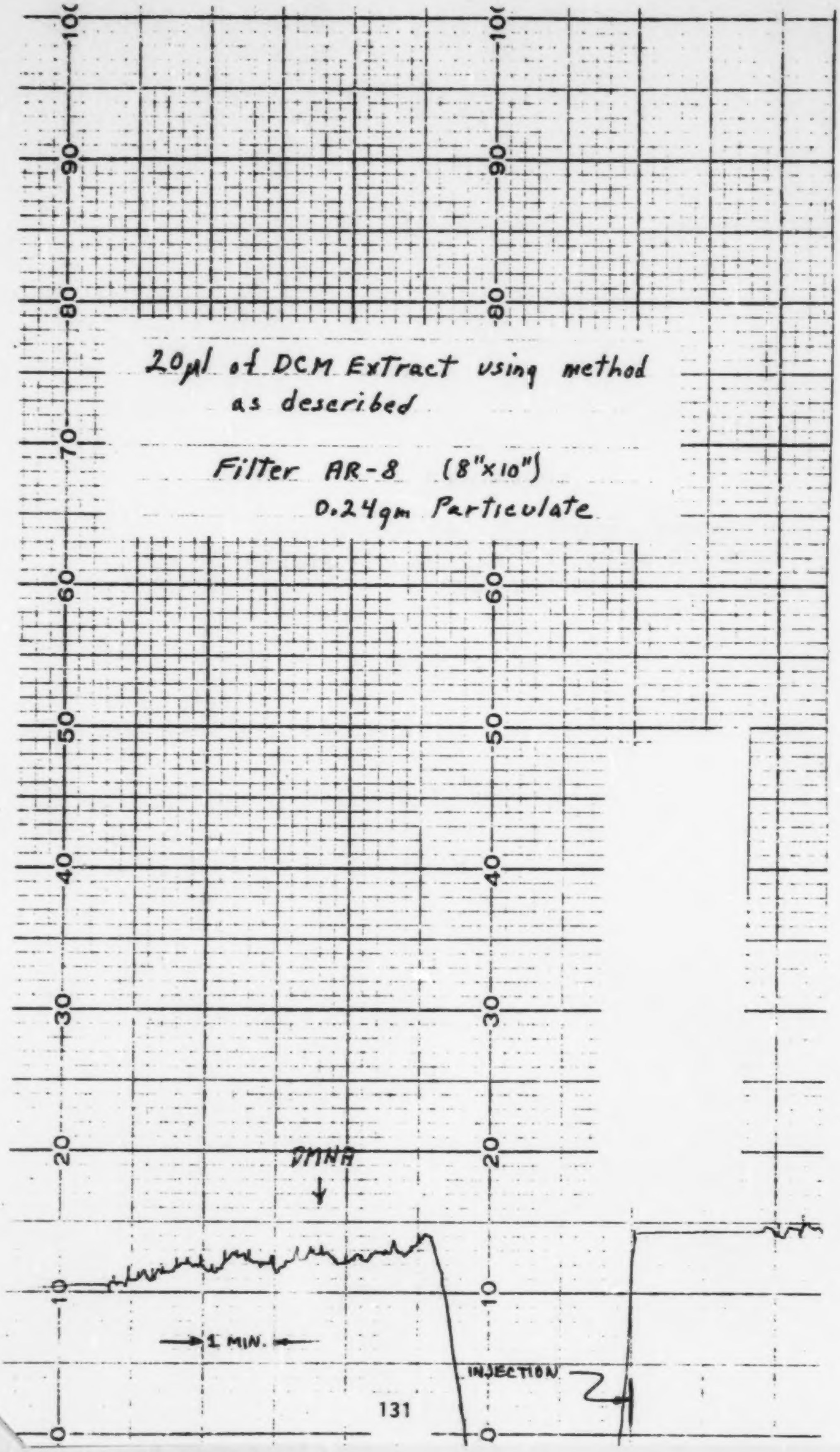
5µl of DIE Extract using method as described

Filter AR-8 (8"x10")
0.24gm Particulate

20µl of DCM Extract using method
as described

70 ml 1% H_3PO_4 spiked with
0.1µg Dimethylnitrosamine





20μl of DCM Extract using method as described

Filter AR-8 (8"x10")
0.24gm Particulate

APPENDIX E

GASEOUS EMISSIONS AND SMOKE DATA ON THE DETROIT DIESEL 6L-71T ENGINE USING FUEL B

```
                 13-MODE FEDERAL DIESEL EMISSION CYCLE

   PROJECT:11-3718-001  DATE OF TEST 1-3-74  TEST NO.1  RUN NO.1
   DETROIT DIESEL 6L-71T  FUEL TYPE EM-195-F
   ------------------------------------------------------------------
   MODE  ENGINE   TORQUE  POWER    FUEL     AIR    EXHAUST  FUEL
         SPEED                     FLOW     FLOW    FLOW     AIR
          RPM     LB-FT    BHP    LB/MIN   LB/MIN  LB/MIN   RATIO
   ------------------------------------------------------------------
     1     480      0.0    0.0      .03     9.44     9.48   .004
     2    1600     15.8    4.8      .18    34.20    34.38   .005
     3    1600    190.8   58.1      .46    36.98    37.44   .013
     4    1600    381.6  116.3      .78    39.80    40.58   .020
     5    1600    574.2  174.9     1.12    44.35    45.47   .025
     6    1600    765.0  233.1     1.50    49.10    50.61   .031
     7     480      0.0    0.0      .04     9.44     9.49   .005
     8    2100    689.8  275.8     1.82    67.99    69.81   .027
     9    2100    516.2  207.2     1.39    61.70    63.10   .023
    10    2100    344.9  137.9     1.01    55.86    56.87   .018
    11    2100    173.3   69.3      .64    51.10    51.74   .013
    12    2100     14.0    5.6      .33    47.93    48.26   .007
    13     480      0.0    0.0      .05     9.45     9.50   .005




-------------------------------------------------------------------------,
MODE   HC     CO+     NO++   WEIGHTED  BSHC      BSCO+    BSNO2++   HUM.

       PPM    PPM     PPM      BHP    G/HP HR   G/HP HR   G/HP HR   GR/LB
-------------------------------------------------------------------------
 1     113     122     178     0.00        R         R         R    28.6
 2     129     130      86      .38    12.20     24.44     26.71    28.6
 3     106      70     282     4.65      .90      1.18      7.84    28.6
 4      64      93     580     9.30      .29       .85      8.74    24.9
 5      76     175     971    13.99      .26      1.20     10.91    27.5
 6      82    1386    1194    18.65      .24      7.92     11.20    31.4
 7      60     119     201     0.00        R         R         R    31.4
 8     108     263    1262    22.06      .36      1.75     13.81    29.7
 9      96     100     928    16.58      .39       .80     12.21    29.7
10      74      82     552    11.03      .40       .89      9.84    31.4
11      80      78     284     5.54      .79      1.54      9.15    31.4
12     100      95     112      .45    11.38     21.53     41.87    29.1
13      92     126     194     0.00        R         R         R    29.1
  CYCLE COMPOSITE    BSHC    =    .489   GRAM/BHP HR
                     BSCO+   =   2.662   GRAM/BHP HR
                     BSNO2++=   11.596   GRAM/BHP HR
              BSHC + BSNO2++=   12.084   GRAM/BHP HR

  +  CONVERTED TO WET BASIS
  ++ CONVERTED TO WET BASIS AND CORRECTED TO 75 GRAINS
     WATER PER LB. DRY AIR
```

13-MODE FEDERAL DIESEL EMISSION CYCLE

PROJECT:11-3718-001 DATE OF TEST 1-5-74 TEST NO.2 RUN NO.1
DETROIT DIESEL 6L-71T FUEL TYPE EM-195-F

MODE	ENGINE SPEED RPM	TORQUE LB-FT	POWER BHP	FUEL FLOW LB/MIN	AIR FLOW LB/MIN	EXHAUST FLOW LB/MIN	FUEL AIR RATIO
1	480	0.0	0.0	.05	9.46	9.51	.005
2	1600	14.0	4.3	.18	33.79	33.97	.005
3	1600	192.6	58.7	.47	37.42	37.89	.013
4	1600	383.4	116.8	.79	40.72	41.51	.019
5	1600	576.0	175.5	1.11	45.17	46.28	.024
6	1600	768.5	234.1	1.51	52.31	53.82	.029
7	480	0.0	0.0	.04	9.44	9.48	.004
8	2100	702.0	280.7	1.82	69.93	71.75	.026
9	2100	527.0	210.7	1.39	62.86	64.25	.022
10	2100	351.9	140.7	1.02	57.51	58.53	.018
11	2100	175.1	70.0	.65	52.40	53.05	.012
12	2100	14.0	5.6	.34	47.94	48.28	.007
13	480	0.0	0.0	.03	9.11	9.14	.004

MODE	HC PPM	CO+ PPM	NO++ PPM	WEIGHTED BHP	BSHC G/HP HR	BSCO+ G/HP HR	BSNO2++ G/HP HR	HUM. GR/LB
1	128	153	155	0.00	R	R	R	27.1
2	148	157	96	.34	15.55	32.93	32.91	27.1
3	116	84	285	4.69	.99	1.43	7.94	27.1
4	56	77	560	9.34	.26	.72	8.60	27.1
5	40	147	903	14.04	.14	1.02	10.29	27.1
6	32	1054	1119	18.73	.10	6.37	11.11	27.1
7	72	112	160	0.00	R	R	R	28.8
8	72	264	1300	22.46	.24	1.77	14.36	28.8
9	60	92	954	16.86	.24	.74	12.57	28.8
10	88	70	567	11.26	.48	.77	10.18	28.8
11	104	64	272	5.60	1.04	1.27	8.90	28.8
12	120	86	135	.45	13.66	19.53	50.34	28.8
13	124	120	136	0.00	R	R	R	28.8

CYCLE COMPOSITE BSHC = .441 GRAM/BHP HR
BSCO+ = 2.328 GRAM/BHP HR
BSNO2++= 11.709 GRAM/BHP HR
BSHC + BSNO2++= 12.150 GRAM/BHP HR

+ CONVERTED TO WET BASIS
++ CONVERTED TO WET BASIS AND CORRECTED TO 75 GRAINS WATER PER LB. DRY AIR

```
                 13-MODE FEDERAL DIESEL EMISSION CYCLE

PROJECT:11-3718-001  DATE OF TEST 1-5-74   TEST NO.2  RUN NO.2
DETROIT DIESEL 6L-71T  FUEL TYPE EM-195-F
------------------------------------------------------------------
MODE  ENGINE   TORQUE   POWER     FUEL      AIR    EXHAUST   FUEL
      SPEED                       FLOW     FLOW      FLOW     AIR
       RPM     LB-FT     BHP    LB/MIN   LB/MIN    LB/MIN   RATIO
------------------------------------------------------------------
  1     480      0.0     0.0       .03     9.07      9.10    .004
  2    1600     14.0     4.3       .18    34.39     34.58    .005
  3    1600    192.6    58.7       .47    37.37     37.84    .012
  4    1600    383.4   116.8       .79    40.52     41.31    .020
  5    1600    576.0   175.5      1.12    45.03     46.14    .025
  6    1600    766.8   233.6      1.50    51.49     52.98    .029
  7     480      0.0     0.0       .03     9.06      9.09    .003
  8    2100    703.8   281.4      1.81    70.35     72.16    .026
  9    2100    528.7   211.4      1.40    62.66     64.06    .022
 10    2100    351.9   140.7      1.03    56.83     57.86    .018
 11    2100    176.8    70.7       .67    52.23     52.90    .013
 12    2100     14.0     5.6       .33    47.84     48.17    .007
 13     460      0.0     0.0       .03     9.09      9.12    .004


-----------------------------------------------------------------------
MODE    HC      CO+     NO++  WEIGHTED   BSHC      BSCO+    BSNO2++  HUM.

        PPM     PPM     PPM     BHP    G/HP HR   G/HP HR   G/HP HR  GR/LB
-----------------------------------------------------------------------
  1     112      75     152     0.00        R         R         R   37.4
  2     160     120      84      .34    17.12     25.50     29.50   37.4
  3     118      94     294     4.69     1.00      1.59      8.20   37.4
  4      84      52     606     9.34      .39       .49      9.26   37.4
  5      88     135    1010    14.04      .31       .93     11.48   37.5
  6      96    1052    1238    18.69      .29      6.27     12.13   37.5
  7     128      91     145     0.00        R         R         R   37.5
  8     104     246    1410    22.51      .35      1.66     15.61   39.1
  9      92      68    1019    16.91      .37       .54     13.34   39.1
 10     103      44     604    11.26      .56       .48     10.74   37.5
 11     112      39     301     5.66     1.11       .76      9.73   37.5
 12     136      64     104      .45    15.44     14.37     38.65   39.1
 13     136      99     152     0.00        R         R         R   39.1
  CYCLE COMPOSITE     BSHC     =     .583   GRAM/BHP HR
                      BSCO+    =    2.098   GRAM/BHP HR
                      BSNO2++=     12.561   GRAM/BHP HR
               BSHC + BSNO2++=     13.144   GRAM/BHP HR

  +   CONVERTED TO WET BASIS
  ++  CONVERTED TO WET BASIS AND CORRECTED TO 75 GRAINS
      WATER PER LB. DRY AIR
```

FEDERAL SMOKE TRACE EVALUATION

Vehicle ______ **Date** 1-7-74 **Evaluated by** KH

Engine Model 6L-71T **Run No.** 1

Acceleration

First Sequence		Second Sequence		Third Sequence	
Interval No.	Smoke %	Interval No.	Smoke %	Interval No.	Smoke %
1	9.2	1	3.5	1	5.0
2	21.5	2	13.0	2	14.0
3	26.0	3	19.5	3	19.0
4	23.0	4	20.0	4	19.5
5	20.7	5	18.0	5	18.5
6	21.0	6	16.5	6	16.3
7	18.3	7	16.5	7	16.5
8	16.0	8	13.0	8	14.5
9	14.8	9	14.0	9	13.0
10	13.0	10	11.0	10	11.0
11	11.0	11	9.5	11	9.0
12	2.5	12	6.5	12	6.3
13	1.8	13	2.5	13	2.0
14	1.5	14	2.5	14	1.5
15	1.5	15	2.2	15	1.5

Total Smoke % 201.8 168.2 167.6

Factor (a) = $\frac{537.6}{45}$ = 11.9 %

Lugging

First Sequence		Second Sequence		Third Sequence	
Interval No.	Smoke %	Interval No.	Smoke %	Interval No.	Smoke %
1	1.0	1	1.5	1	1.5
2	1.2	2	1.5	2	1.5
3	1.2	3	1.5	3	1.5
4	1.2	4	1.5	4	1.5
5	1.2	5	1.5	5	1.5

Total Smoke % 5.8 7.5 7.5

Factor (b) = $\frac{20.8}{15}$ = 1.4 %

Peak Readings

First Sequence		Second Sequence		Third Sequence	
Interval No.	Smoke %	Interval No.	Smoke %	Interval No.	Smoke %
1	26.0	1	20.0	1	19.5
2	23.0	2	19.5	2	19.0
3	21.5	3	18.0	3	18.5

Total Smoke % 70.5 57.5 57.0

Factor (c) = $\frac{185}{9}$ = 20.6 %

FEDERAL SMOKE TRACE EVALUATION

Vehicle ____________ **Date** 1-7-74 **Evaluated by** KH

Engine Model 6L-71T **Run No.** 2

Acceleration

First Sequence		Second Sequence		Third Sequence	
Interval No.	Smoke %	Interval No.	Smoke %	Interval No.	Smoke %
1	4.0	1	5.0	1	9.0
2	12.5	2	15.0	2	21.5
3	21.5	3	21.5	3	21.0
4	20.0	4	22.0	4	18.5
5	20.0	5	19.5	5	18.5
6	20.5	6	19.5	6	18.0
7	21.0	7	18.0	7	16.0
8	18.0	8	16.5	8	16.0
9	17.0	9	15.0	9	13.5
10	15.0	10	13.5	10	11.0
11	11.5	11	10.0	11	8.5
12	8.5	12	7.8	12	6.0
13	2.5	13	2.0	13	4.5
14	2.5	14	2.3	14	4.0
15	2.5	15	2.0	15	3.5
Total Smoke %	197.0		189.6		189.5

Factor (a) = $\frac{576.1}{45}$ = 12.8%

Lugging

First Sequence		Second Sequence		Third Sequence	
Interval No.	Smoke %	Interval No.	Smoke %	Interval No.	Smoke %
1	2.2	1	2.2	1	1.5
2	2.2	2	2.2	2	1.5
3	2.2	3	2.5	3	1.5
4	2.5	4	2.5	4	1.5
5	2.5	5	2.5	5	1.9
Total Smoke %	11.6		11.9		7.9

Factor (b) = $\frac{31.4}{15}$ = 2.1%

Peak Readings

First Sequence		Second Sequence		Third Sequence	
Interval No.	Smoke %	Interval No.	Smoke %	Interval No.	Smoke %
1	21.5	1	22.0	1	21.5
2	21.0	2	21.5	2	21.0
3	20.5	3	19.5	3	18.5
Total Smoke %	63.0		63.0		61.0

Factor (c) = $\frac{187}{9}$ = 20.8%

FEDERAL SMOKE TRACE EVALUATION

Vehicle ________ **Date** 1-7-74 **Evaluated by** KH
Engine Model 6L-71T **Run No.** 3

Accelerations

First Sequence		Second Sequence		Third Sequence	
Interval No.	**Smoke %**	**Interval No.**	**Smoke %**	**Interval No.**	**Smoke %**
1	9.0	1	5.0	1	15.0
2	21.0	2	16.0	2	25.0
3	23.5	3	24.0	3	25.0
4	19.0	4	19.0	4	22.0
5	19.0	5	17.5	5	20.0
6	18.5	6	17.5	6	19.3
7	16.5	7	17.0	7	17.0
8	16.0	8	16.5	8	17.0
9	14.0	9	15.0	9	14.5
10	11.8	10	12.0	10	12.0
11	8.5	11	10.0	11	9.0
12	6.5	12	7.0	12	6.5
13	2.6	13	2.7	13	2.5
14	2.6	14	3.2	14	2.8
15	2.6	15	3.0	15	2.8
Total Smoke %	191.1		185.4		210.4

Factor (a) = $\frac{586.9}{45}$ = 13.0 %

Lugging

First Sequence		Second Sequence		Third Sequence	
Interval No.	**Smoke %**	**Interval No.**	**Smoke %**	**Interval No.**	**Smoke %**
1	1.5	1	2.0	1	1.7
2	1.5	2	2.0	2	1.8
3	1.5	3	2.0	3	1.8
4	1.8	4	2.0	4	2.0
5	1.8	5	2.0	5	2.5
Total Smoke %	8.1		10.0		9.8

Factor (b) = $\frac{27.9}{15}$ = 1.9 %

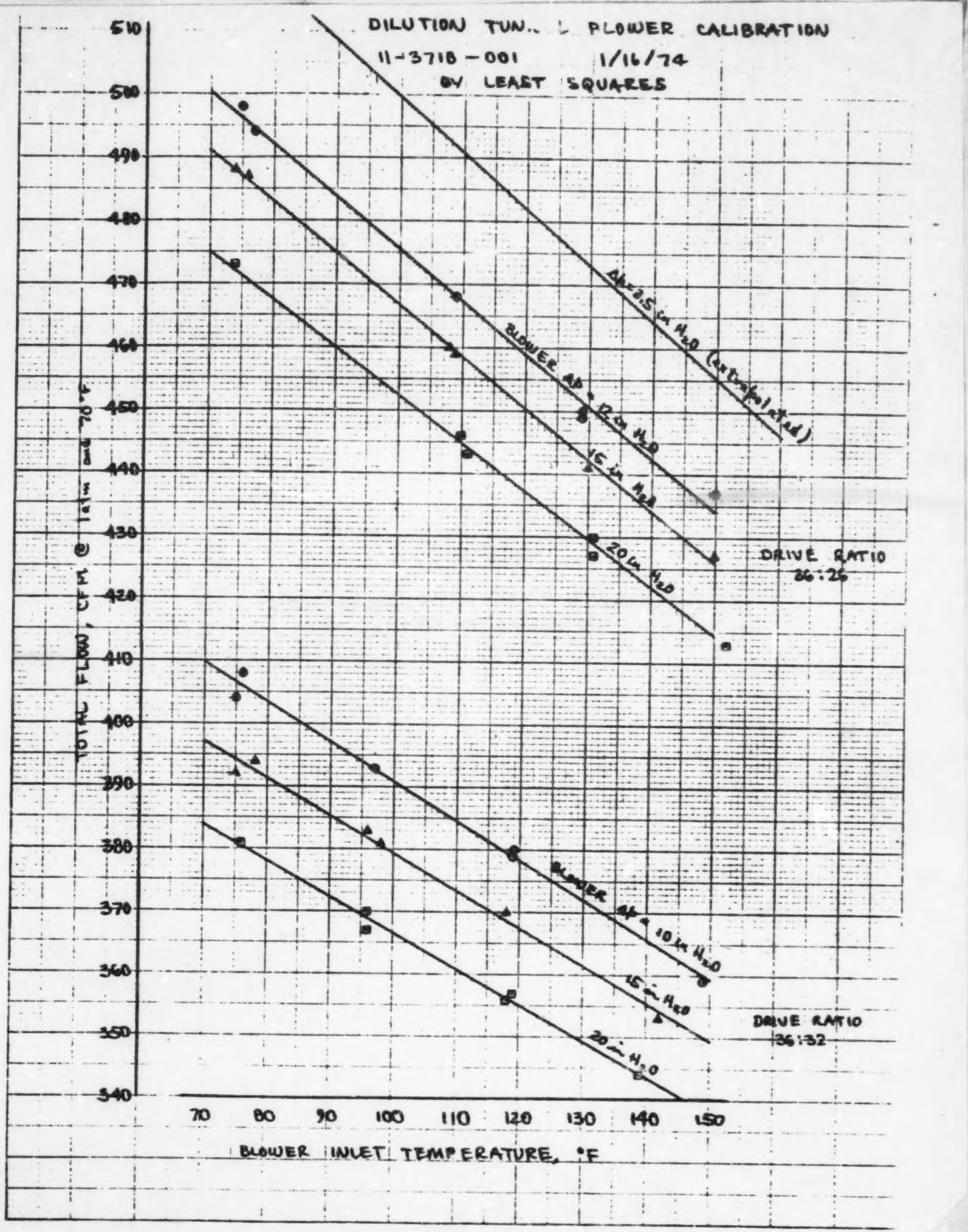
Peak Readings

First Sequence		Second Sequence		Third Sequence	
Interval No.	**Smoke %**	**Interval No.**	**Smoke %**	**Interval No.**	**Smoke %**
1	23.5	1	24.0	1	25.0
2	21.0	2	19.0	2	25.0
3	19.0	3	17.5	3	22.0
Total Smoke %	63.5		60.5		72.0

Factor (c) = $\frac{196}{9}$ = 21.8 %

APPENDIX F

CALIBRATION AND PROFILE ANALYSIS OF DILUTION TUNNEL


DILUTION TUN.. L PLOWER CALIBRATION
11-3718-001 1/16/74
BY LEAST SQUARES
ΔP=2.5 in H_2O (extrapolated)
BLOWER ΔP = 12 in H_2O
15 in H_2O
20 in H_2O
DRIVE RATIO 36:25
BLOWER ΔP = 10 in H_2O
15 in H_2O
20 in H_2O
DRIVE RATIO 36:32
TOTAL FLOW, CFM @ 1 atm and 70°F
510
500
490
480
470
460
450
440
430
420
410
400
390
380
370
360
350
340
70
80
90
100
110
120
130
140
150
BLOWER INLET TEMPERATURE, °F

11-3718-001

DATE 1/16/74

MOTOR PULLEY 36 BLOWER PULLEY 26

CALCULATIONS - DILUTION TUNNEL BLOWER CALIBRATION

BLOWER INLET TEMP., °F		BLOWER	BLOWER	LAMINAR FLOW ELEMENT				BLOWER
TARGET	ACTUAL	Δp, in H_2O	REV/min	Q, UNCORR.	P CORR.	T CORR.	Q, CORR.	V/R, ft³/rev
75	75	12	1631	520.	0.9741	0.9834	498.	0.324
75	74	15	1628	509.	0.9746	0.9834	488.	0.317
75	74	20	1618	493.	0.9751	0.9834	473.	0.315
100	109	12	1634	548.	0.9746	0.8766	468.	0.322
100	109	15	1627	537.	0.9748	0.8766	459.	0.320
100	111	20	1620	523.	0.9753	0.8686	443.	0.315
125	129	12	1634	563.	0.9748	0.8179	449.	0.320
125	130	15	1629	555.	0.9751	0.8155	441.	0.318
125	131	20	1621	540.	0.9756	0.8107	427.	0.314
150	150	12	1635	584.	0.9751	0.7675	437.	0.322
150	150	15	1629	574.	0.9753	0.7632	427.	0.319
150	152	20	1621	558.	0.9758	0.7589	413.	0.315
75	77	12	1631	517.	0.9746	0.9802	494.	0.322
75	76	15	1627	510.	0.9748	0.9802	487.	0.320
100	108	15	1627	538.	0.9751	0.8766	460.	0.320
100	110	20	1620	527.	0.9751	0.8686	446.	0.317
125	129	12	1633	564.	0.9748	0.8179	450.	0.321
125	131	20	1619	542.	0.9753	0.8131	430.	0.317

ATMOSPHERIC PRESSURE 29.44 in Hg

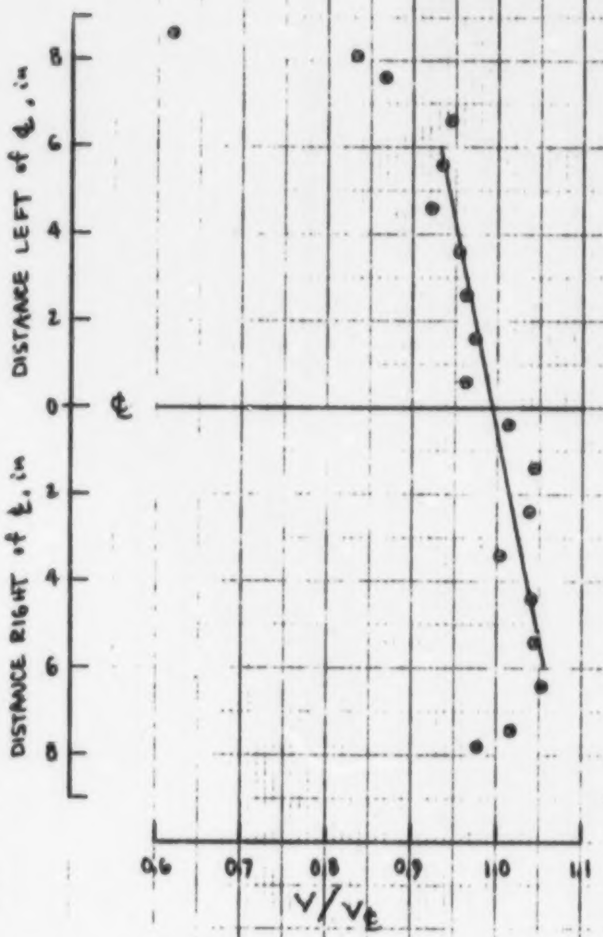
DATE 1/10/74

MOTOR PULLEY 36 BLOWER PULLEY 32

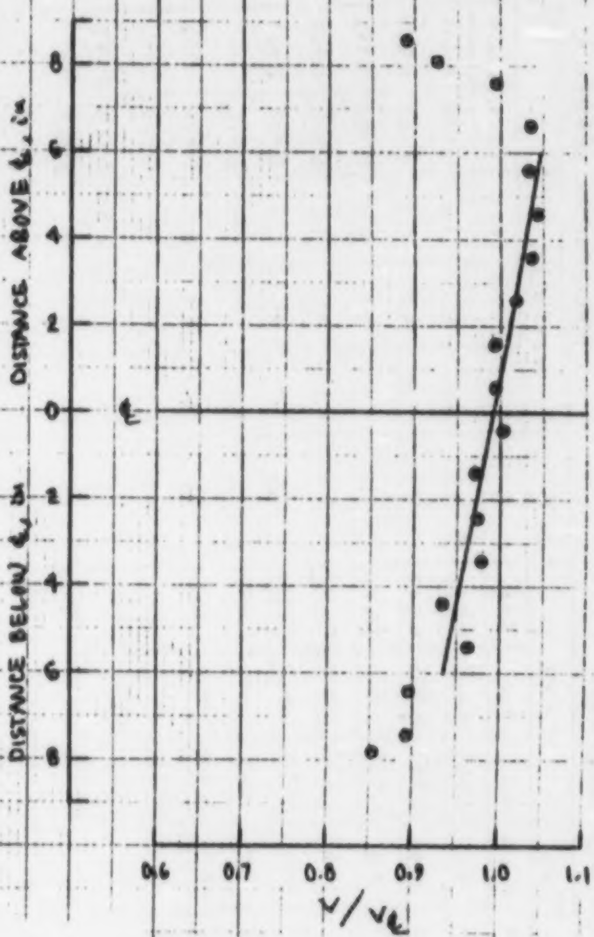
CALCULATIONS - DILUTION TUNNEL BLOWER CALIBRATION

BLOWER INLET TEMP., °F		BLOWER	BLOWER	LAMINAR FLOW ELEMENT			
TARGET	ACTUAL	Δp, in H_2O	REV/min	Q, UNCORR.	P CORR.	T CORR.	Q, CORR.
75	76	10	1334	426.	0.9764	0.9802	408.
75	78	15	1330	414.	0.9769	0.9737	394.
75	76	20	1325	398.	0.9771	0.9802	381.
100	97	10	1336	441.	0.9766	0.9129	393.
100	96	15	1332	428.	0.9769	0.9158	363.
100	96	20	1326	415.	0.9771	0.9129	370.
125	119	10	1337	458.	0.9766	0.8477	379.
125	118	15	1332	447.	0.9771	0.8477	370.
125	119	20	1328	432.	0.9776	0.8452	357.
150	149	10	1336	481.	0.9769	0.7632	359.
150	142	15	1332	457.	0.9771	0.7898	353.
150	139	20	1327	440.	0.9776	0.7990	344.
75	75	10	1336	419.	0.9766	0.9867	404.
75	75	15	1332	407.	0.9769	0.9867	392.
100	98	15	1331	427.	0.9769	0.9129	381.
100	96	20	1325	410.	0.9771	0.9158	367.
125	119	10	1335	459.	0.9769	0.8477	380.
125	118	20	1327	432.	0.9774	0.8426	356.

ATMOSPHERIC PRESSURE 29.42 in Hg



HORIZONTAL VELOCITY PROFILE AT SAMPLING STATION



VERTICAL VELOCITY PROFILE AT SAMPLING STATION

2/12/74

VELOCITY PROFILE CALCULATIONS

VERTICAL PROFILE

inches above ℄	V, ft/sec		V/V℄		
	Run 1	Run 3	Run 1	Run 3	Avg.
8.6	6.4	9.5	0.867	0.915	0.891
8.1	5.55	10.0	0.891	0.963	0.927
7.6	6.1	10.5	0.979	1.012	0.996
6.6	6.3	11.0	1.011	1.060	1.036
5.6	6.4	10.8	1.027	1.040	1.034
4.6	6.5	—	1.043	—	1.043
3.6	6.5	10.7	1.043	1.031	1.037
2.6	6.35	—	1.019	—	1.019
1.6	6.2	10.3	0.995	0.992	0.994
0.6	6.2	—	0.995	—	0.995
-0.4	6.25	10.4	1.003	1.002	1.003
-1.4	6.05	—	0.971	—	0.971
-2.4	6.0	10.2	0.963	0.983	0.973
-3.4	6.1	—	0.979	—	0.979
-4.4	5.8	9.7	0.931	0.934	0.933
-5.4	6.0	—	0.963	—	0.963
-6.4	5.6	9.3	0.899	0.896	0.897
-7.4	5.55	9.3	0.891	0.896	0.893
-7.8	5.35	8.8	0.859	0.848	0.853
V℄	6.23	10.38			

HORIZONTAL PROFILE

inches left of ℄	V, ft/sec			V/V℄			
	Run 2	Run 4	Run 5	Run 2	Run 4	Run 5	Avg.
8.6	5.45	6.1	4.0	0.558	0.611	0.687	0.619
8.1	7.05	8.5	5.4	0.722	0.852	0.928	0.834
7.6	7.4	9.0	5.5	0.758	0.902	0.945	0.868
6.6	8.9	9.6	5.6	0.912	0.962	0.962	0.945
5.6	8.9	9.6	5.4	0.912	0.962	0.928	0.934
4.6	9.0	—	—	0.922	—	—	0.922
3.6	9.5	10.0	5.2	0.973	1.002	0.893	0.956
2.6	9.4	—	—	0.963	—	—	0.963
1.6	9.6	9.9	5.5	0.984	0.992	0.945	0.974
0.6	9.4	—	—	0.963	—	—	0.963
-0.4	10.0	10.0	5.9	1.025	1.002	1.014	1.014
-1.4	10.2	—	—	1.045	—	—	1.045
-2.4	10.3	10.3	6.0	1.056	1.032	1.031	1.039
-3.4	9.8	—	—	1.004	—	—	1.004
-4.4	10.5	10.3	5.9	1.076	1.032	1.014	1.041
-5.4	10.2	—	—	1.045	—	—	1.045
-6.4	10.4	10.4	6.1	1.066	1.042	1.048	1.052
-7.4	10.5	9.8	5.8	1.076	0.982	0.997	1.018
-7.8	10.0	10.0	5.3	1.025	1.002	0.911	0.979
	9.76	9.98	5.82				

- to get straight lines across duct center, use least squares on all points inside ≈ 7-inch radius (14 for each profile)

11-3718-001
2/12/14

let $U = V/V_{℄}$ $U = a + bx$

let x = distance from ℄, inches — up and left are positive

$n = 14$ $a = \bar{U} - b\bar{x}$ $b = \dfrac{n\sum x_i U_i - \sum x_i \sum U_i}{n\sum x_i^2 - (\sum x_i)^2}$

VERTICAL PROFILE		HORIZONTAL PROFILE	
x	U	x	U
6.6	1.036	6.6	0.945
5.6	1.034	5.6	0.934
4.6	1.043	4.6	0.922
3.6	1.037	3.6	0.956
2.6	1.019	2.6	0.963
1.6	0.994	1.6	0.974
0.6	0.995	0.6	0.963
-0.4	1.003	-0.4	1.014
-1.4	0.971	-1.4	1.045
-2.4	0.973	-2.4	1.039
-3.4	0.979	-3.4	1.004
-4.4	0.933	-4.4	1.041
-5.4	0.963	-5.4	1.045
-6.4	0.897	-6.4	1.052

$\bar{x} = 0.10$
$\bar{U} = 0.9912$
$\sum x_i = 1.4$
$\sum U_i = 13.877$
$\sum x_i^2 = 227.64$
$\sum x_i U_i = 3.5252$

$\bar{x} = 0.10$
$\bar{U} = 0.9926$
$\sum x_i = 1.4$
$\sum U_i = 13.897$
$\sum x_i^2 = 227.64$
$\sum x_i U_i = -0.9418$

$b = 0.009396$
$a = 0.9903$
$\therefore U = 0.9903 + 0.009396\,x$

$b = -0.01025$
$a = 0.994$
$U = 0.994 - 0.01025\,x$

$\therefore U_{7.0} = 1.056$
$= 0.925$

$U_{7.0} = 0.922$
$U_{-7.0} = 1.066$

Integration of average velocity profiles (from summary of 2/12)

$$V_b = \frac{2}{R^2}\int_0^R V r\,dr = \frac{2}{R^2}\sum_{i=1}^{n} (\overline{V_r})_i (\Delta r)_i$$

V_b (corrected avg) = 0.898 $V_{\mathfrak{c}}$

$\therefore V_{\mathfrak{c}}/V_b \cong 1.114$ $\quad V_{max}/V_b \cong 1.16$

TOP					
r	V	Vr	$\overline{Vr}$	Δr	$\overline{Vr}$ Δr
8.85	0	0	3.8313	0.25	0.9578
8.6	0.891	7.6626	7.5856	0.5	3.7928
8.1	0.927	7.5087	7.5392	0.5	3.7696
7.6	0.996	7.5696	7.2036	1.0	7.2036
6.6	1.036	6.8376	6.3140	1.0	6.3140
5.6	1.034	5.7904	5.2941	1.0	5.2941
4.6	1.043	4.7978	4.2655	1.0	4.2655
3.6	1.037	3.7332	3.1913	1.0	3.1913
2.6	1.019	2.6494	2.1199	1.0	2.1199
1.6	0.994	1.5904	1.0937	1.0	1.0937
0.6	0.995	0.597	0.2985	0.6	0.1791
0	1.000	0			
				Σ =	38.1814

V_b(top) = 0.9750

BOTTOM					
r	V	Vr	$\overline{Vr}$	Δr	$\overline{Vr}$ Δr
8.85	0	0	3.3267	1.05	3.4930
7.8	0.853	6.6534	6.6308	0.4	2.6523
7.4	0.893	6.6082	6.1745	1.0	6.1745
6.4	0.897	5.7408	5.4495	1.0	5.4495
5.4	0.963	5.2002	5.008	1.0	5.008
4.4	0.933	4.1052	3.7169	1.0	3.7169
3.4	0.979	3.3286	2.8319	1.0	2.8319
2.4	0.973	2.3352	1.8473	1.0	1.8473
1.4	0.971	1.3594	0.8803	1.0	0.8803
0.4	1.003	0.4012	0.2006	0.4	0.0802
0	1.000	0			
				Σ =	31.8338

V_b(bottom) = 0.8129

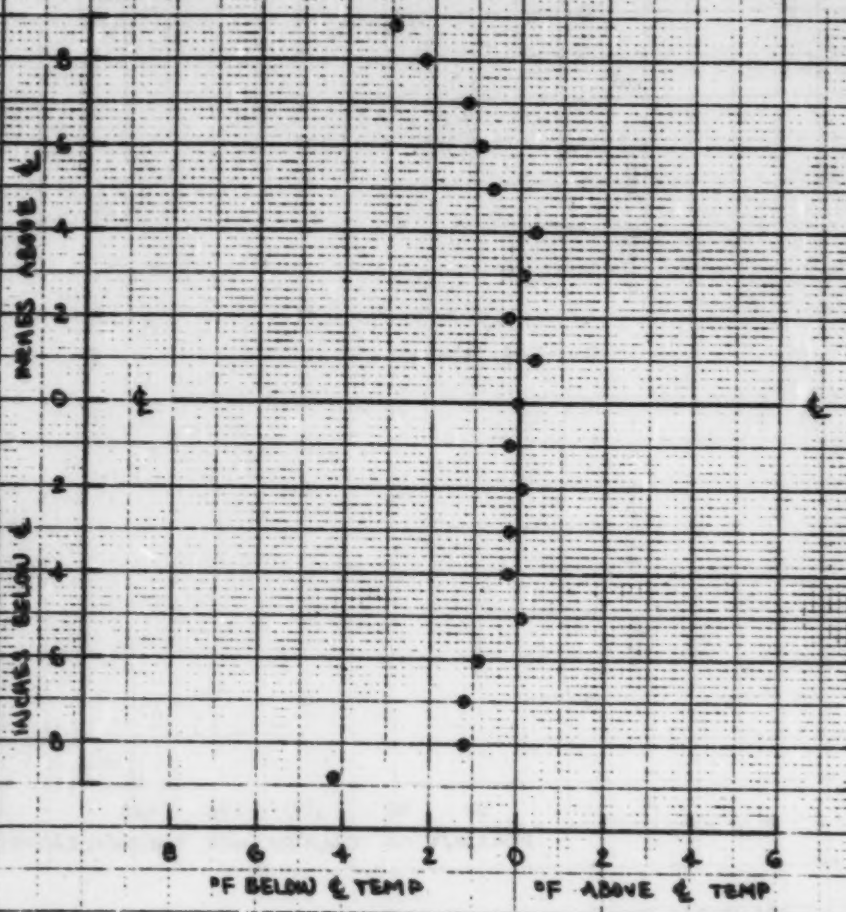
LEFT					
r	V	Vr	$\overline{Vr}$	Δr	$\overline{Vr}$ Δr
8.85	0	0	2.6617	0.25	0.6654
8.6	0.619	5.3234	6.0394	0.5	3.0197
8.1	0.834	6.7554	6.6761	0.5	3.3380
7.6	0.868	6.5968	6.4169	1.0	6.4169
6.6	0.945	6.2370	5.7337	1.0	5.7337
5.6	0.934	5.2304	4.7358	1.0	4.7358
4.6	0.922	4.2412	3.8414	1.0	3.8414
3.6	0.956	3.4416	2.9727	1.0	2.9727
2.6	0.963	2.5038	2.0311	1.0	2.0311
1.6	0.974	1.5584	1.0681	1.0	1.0681
0.6	0.963	0.5778	0.2889	0.6	0.1733
0	0.983	0			
				Σ =	33.9962

V_b(left) = 0.8681 (0.8831 corrected)

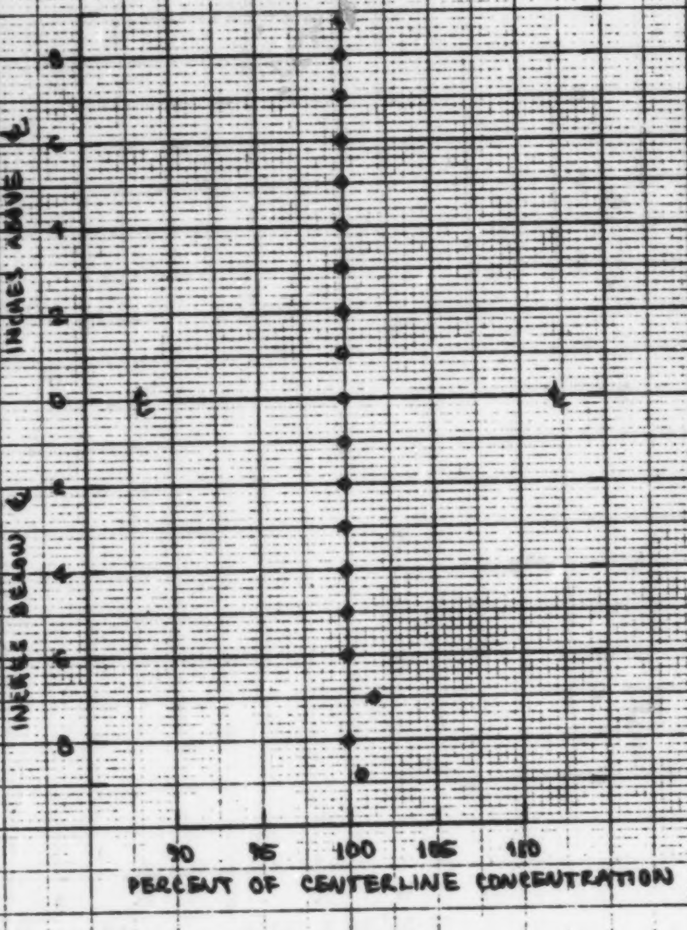
RIGHT					
r	V	Vr	$\overline{Vr}$	Δr	$\overline{Vr}$ Δr
8.85	0	0	3.8181	1.05	4.0090
7.8	0.979	7.6362	7.5847	0.4	3.0339
7.4	1.018	7.5332	7.1330	1.0	7.1330
6.4	1.052	6.7328	6.1879	1.0	6.1879
5.4	1.045	5.6430	5.0755	1.0	5.0755
4.4	1.041	4.5804	3.9970	1.0	3.9970
3.4	1.004	3.4136	2.9536	1.0	2.9536
2.4	1.039	2.4936	1.9783	1.0	1.9783
1.4	1.045	1.4630	0.9343	1.0	0.9343
0.4	1.014	0.4056	0.2028	0.4	0.0811
0	0.983	0			
				Σ =	35.3036

V_b(right) = 0.9035 (0.9191 corrected)

6



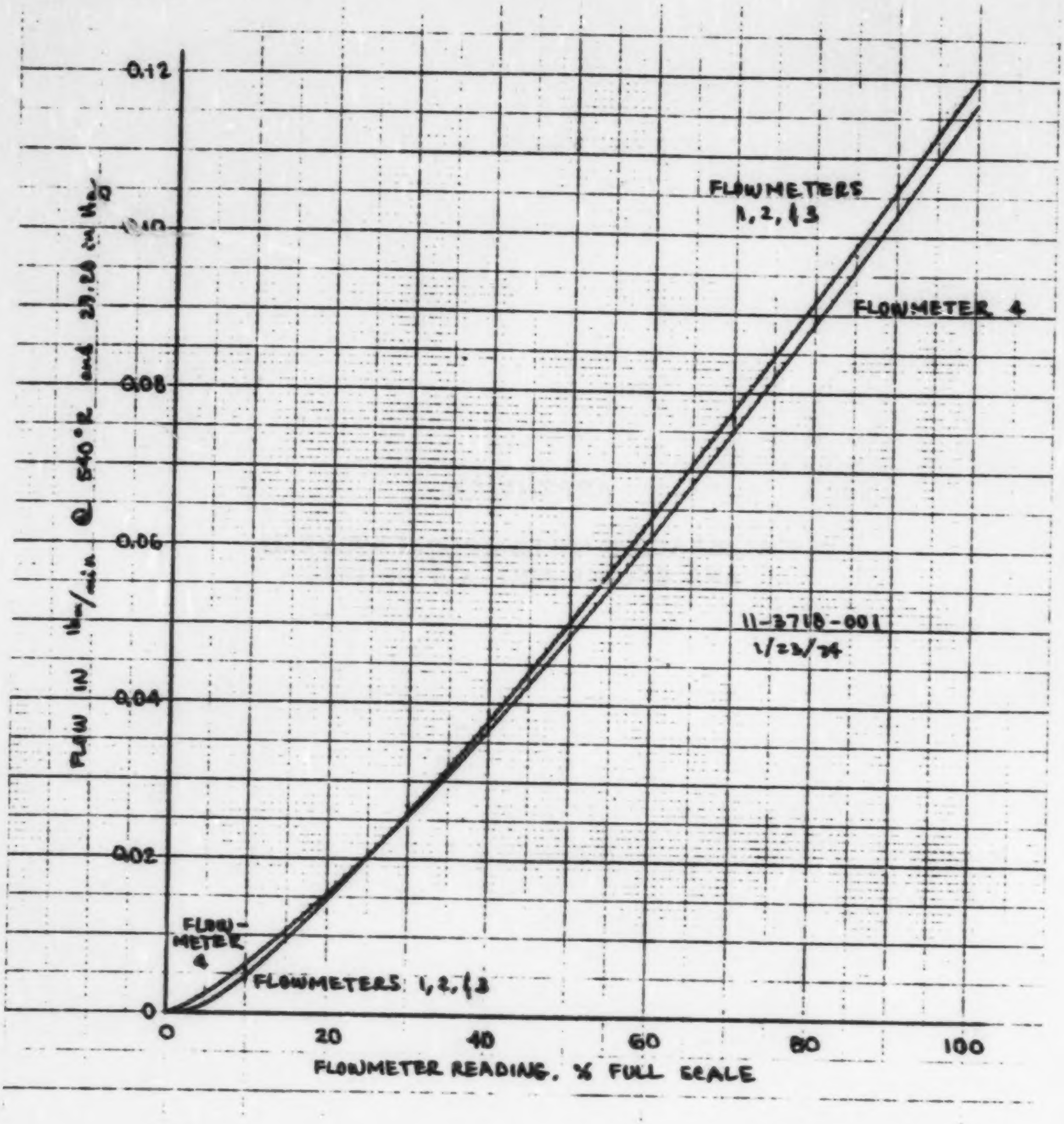
DILUTION TUNNEL TEMPERATURE PROFILE, AVERAGE OF THREE OPERATING CONDITIONS



DILUTION TUNNEL CONCENTRATION PROFILE USING 6L-71T ENGINE AS GAS GENERATOR (VERTICAL)

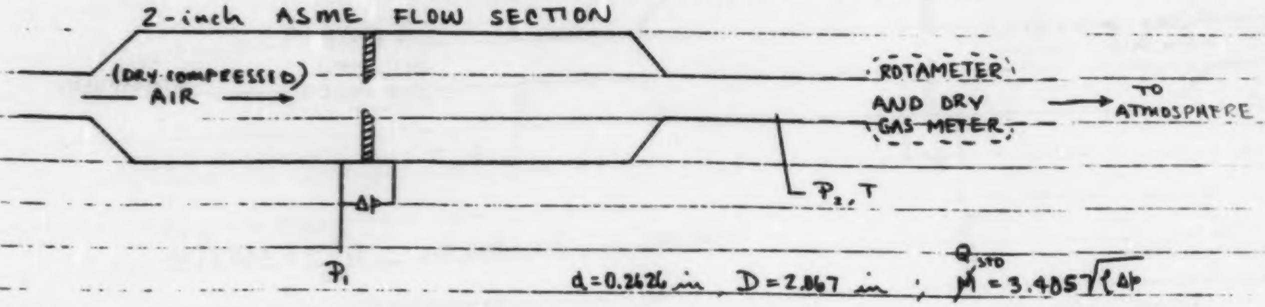
APPENDIX G

CALIBRATION OF SAMPLING SYSTEMS AND ENGINE AIRFLOW ORIFICE

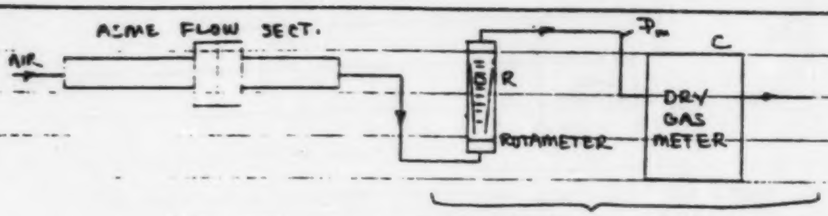

FLOW IN lbm/min @ 540°R and 29.26 in HgO
0.12
0.10
0.08
0.06
0.04
0.02
0
0
20
40
60
80
100
FLOWMETER READING, % FULL SCALE
FLOWMETERS 1, 2, & 3
FLOWMETER 4
11-3710-001
1/23/74
FLOW-METER 4
FLOWMETERS 1, 2, & 3

DATE 1/18/74

CALIBRATION OF FLOW MEASURING DEVICES (47 mm DIA FILT.)


2-inch ASME FLOW SECTION
(DRY COMPRESSED)
AIR
ROTAMETER
AND DRY
GAS METER
TO
ATMOSPHERE
Δp
P_1
P_2, T

$d = 0.2626$ in , $D = 2.067$ in ; $\overset{Q_{STD}}{\cancel{\dot{M}}} = 3.4057\sqrt{\rho \Delta p}$


ASME FLOW SECT.
AIR
R
ROTAMETER
P_m
C
DRY
GAS
METER

THIS PART OF SYSTEM TO
BE CONNECTED IN FINAL
CONFIGURATION FOR CALIB.

ATMOSPHERIC PRESSURE = p_a = 29.14 in Hg   METER No. 1

	RUN 1							RUN 2						
R	C (ft³)	time (sec)	P_m	P_1	Δp	t	P_2	C (ft³)	time (sec)	P_m	P_1	Δp	t	P_2
10	0.2	131.8	0	3	——	84	2	0.2	123.7	0	3	0.004	84	1
30	0.8	126.1	2.5	12	0.145	84	5	0.8	122.5	1.5	14	0.154	84	10
50	1.4	120.9	4.5	29	0.494	84	26	1.5	127.2	3.5	31	0.510	84	28
70	2.2	124.6	8.5	60	1.111	84	56	2.2	124.6	7.5	62	1.108	84	57
90	2.9	121.5	13.5	104	1.922	84	96	2.9	121.5	13.5	104	1.922	84	97

R is rotameter reading   C is ft³ counted on dry gas meter for about 120 sec

t is temperatures in °F P_m, P_1 & P_2 are in inches of H_2O

Δp is in inches of H_2O BY MICROMANOMETER $\rho_1 = 1.326\, p_1/T_1$

R	p_1	p_m	Δp	p_2	T	$\dot{M}$, lb/~~[illegible]~~	Q, SCFM @ 70°F & 1 atm	Q DGM (corr.)
10	29.25	29.14	0.004	29.36	544	0.004 (0.00440)	0.06 (0.0588)	0.0891
30	30.10	29.29	0.150	29.69	544	0.0274	0.366	0.368
50	31.35	29.43	0.502	31.13	544	0.0511	0.683	0.672
70	33.63	29.73	1.110	33.29	544	0.0787	1.051	1.026
90	36.79	30.13	1.922	36.24	544	0.108	1.447	1.405

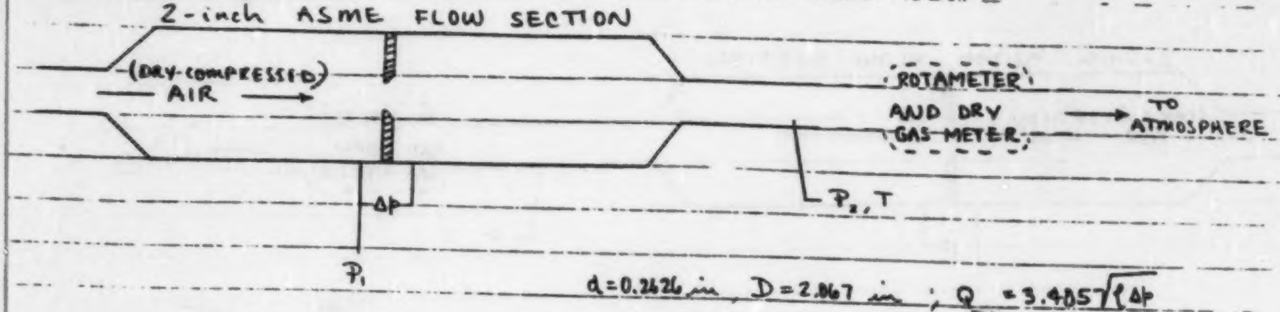
(1/21/74

dry gas meter factor = 1.027

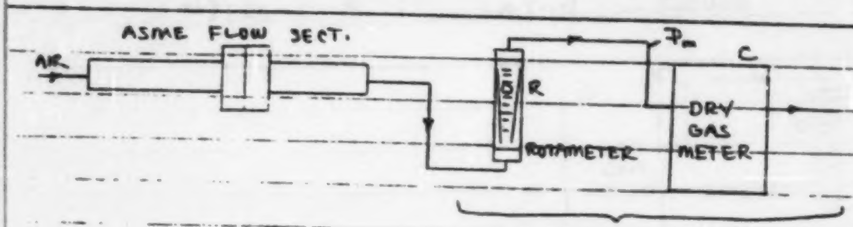
p_1 & p_2 are in inches of H_g absolute

DATE 1/18/74

CALIBRATION OF FLOW MEASURING DEVICES (47 mm DIA FILT.)


2-inch ASME FLOW SECTION
(DRY COMPRESSED)
AIR
ROTAMETER
AND DRY
GAS METER
TO
ATMOSPHERE
Δp
P_1
P_2, T

$d = 0.2626$ in, $D = 2.067$ in ; $Q_{STD} = 3.4057\sqrt{\rho\Delta p}$


ASME FLOW SECT.
AIR
R
ROTAMETER
P_m
C
DRY
GAS
METER

THIS PART OF SYSTEM TO
BE CONNECTED IN FINAL
CONFIGURATION FOR CALIB.

ATMOSPHERIC PRESSURE = p_a = 29.13 in Hg METER No. 2

	RUN 1							RUN 2						
R	C (ft³)	time (sec)	P_m	P_1	Δp	t	P_2	C (ft³)	time (sec)	P_m	P_1	Δp	t	P_2
10	0.2	130.1	0.4	3	0.005	84	2	0.2	129.0	0.4	4	0.004	84	2
30	0.8	129.2	1.6	12	0.139	84	10	0.8	126.0	—	13	0.143	84	11
50	1.4	122.4	4.0	29	0.496	84	26	1.4	120.9	4.2	31	0.507	84	27
70	2.2	131.0	8.5	60	1.105	84	56	2.2	126.2	8.4	61	1.107	84	56
90	2.9	122.8	14.5	103	1.925	84	96	2.9	121.6	14.5	103	1.944	84	97

R is rotameter reading C is ft³ counted on dry gas meter for about 120 sec

t is temperature in °F P_m, P_i & P_2 are in inches of H_2O

Δp is in inches of H_2O BY MICROMANOMETER $\rho_1 = 1.326\ P_1/T_1$

R	p_1	p_m	Δp	p_2	T	$\dot{m}$, lbm/min	Q, SCFM @ 70°F & 1 atm	Q DGM (corr.)
10	29.39	29.16	0.0045	29.28	544	0.004 (0.00469)	0.06 (0.0626)	0.0880
30	30.05	29.25	0.141	29.90	544	0.0265	0.354	0.358
50	31.34	29.43	0.502	31.08	544	0.0511	0.682	0.662
70	33.58	29.75	1.106	33.25	544	0.0785	1.049	0.994
90	36.70	30.20	1.934	36.23	544	0.109	1.450	1.400

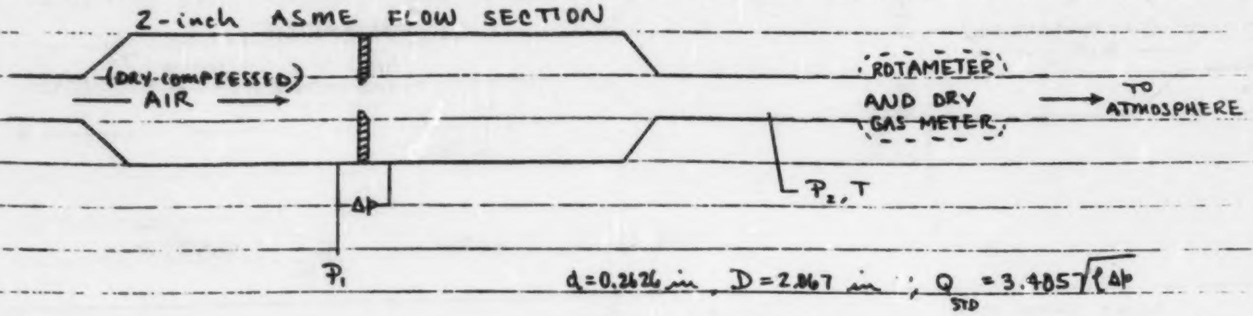
(1/21/74)

Dry gas meter factor = 1.046

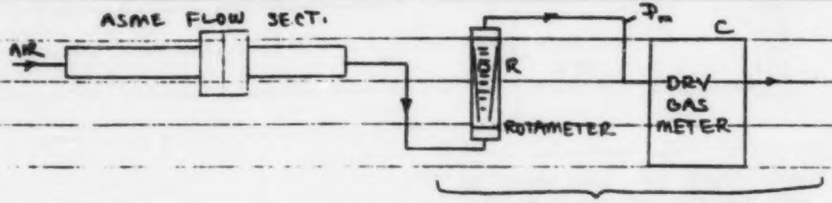
p_m & p_2 are in inches of Hg absolute

DATE 1/21/77

CALIBRATION OF FLOW MEASURING DEVICES (47 mm DIA FILT.)


2-inch ASME FLOW SECTION
(DRY-COMPRESSED) AIR
ROTAMETER AND DRY GAS METER
TO ATMOSPHERE
Δp
P_1
P_2, T

$d = 0.2626$ in, $D = 2.067$ in ; $Q_{STD} = 3.4857\sqrt{\rho_1 \Delta p}$


ASME FLOW SECT.
AIR
R
ROTAMETER
P_m
C
DRY GAS METER

THIS PART OF SYSTEM TO BE CONNECTED IN FINAL CONFIGURATION FOR CALIB.

ATMOSPHERIC PRESSURE = p_a = 29.34 in Hg METER No. 3

	RUN 1							RUN 2						
R	C (ft³)	time (sec)	P_m	P_1	Δp	t	P_2	C (ft³)	time (sec)	P_m	P_1	Δp	t	P_2
10	0.2	113.3	0.3	2.5	0.007	80	2	0.2	122.7	0.2	3	0.006	80	1.8
30	0.8	127.1	1.5	13	0.144	80	10	0.8	126.8	1.5	13	0.152	80	11
50	1.4	122.0	4.2	32	0.478	80	28	1.5	127.8	4.2	34	0.516	80	30
70	2.1	123.1	8.5	64	1.065	80	60	2.1	122.3	8.6	67	1.072	80	62
85	2.7	125.5	13.5	100	1.622	80	94	2.7	125.3	13.5	100	1.624	80	94

R is rotameter reading C is ft³ counted on dry gas meter for about 120 sec

t is Temperatures in °F P_m, P_1 & P_2 are in inches of H_2O

Δp is in inches of H_2O BY MICROMANOMETER $\rho_1 = 1.326\, p_1/T_1$

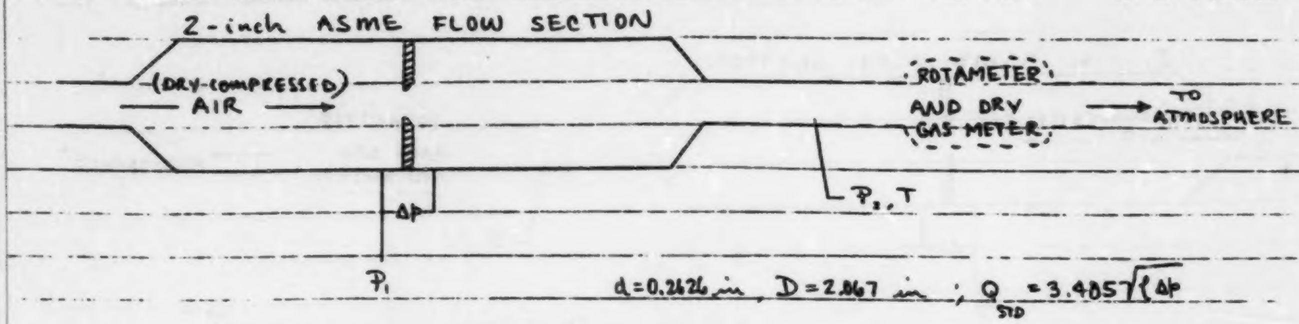
R	p_1	p_m	Δp	p_2	T	$\dot{m}$, lbm/min	Q, SCFM @ 70°F & 1 atm	Q DGM (corr.)
10	29.54	29.36	0.0065	29.48	540	0.006 (0.00567)	0.08 (0.0757)	0.0979
30	30.30	29.45	0.148	29.42	540	0.0274	0.366	0.363
50	31.77	29.65	0.497	31.47	540	0.0514	0.686	0.677
70	34.16	29.97	1.068	33.83	540	0.0781	1.043	1.010
85	36.69	30.33	1.623	36.25	540	0.0998	1.333	1.285

Dry gas meter factor = 1.035

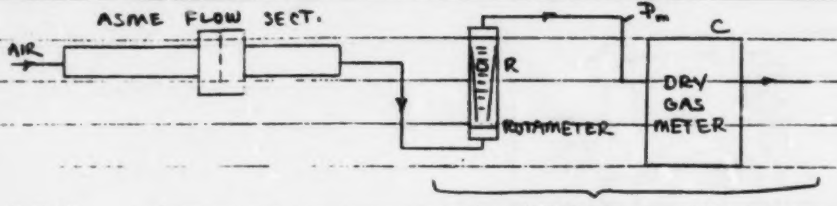
& p_2 are in inches of Hg absolute

DATE 1/21/74

CALIBRATION OF FLOW MEASURING DEVICES (47 mm DIA FILT.)


2-inch ASME FLOW SECTION
(DRY-COMPRESSED)
AIR
ROTAMETER AND DRY GAS METER
TO ATMOSPHERE
Δp
P_1
P_2, T

$d = 0.2626$ in, $D = 2.067$ in ; $Q_{STD} = 3.4857\sqrt{\rho_1 \Delta p}$


ASME FLOW SECT.
AIR
R
ROTAMETER
P_m
C
DRY GAS METER

THIS PART OF SYSTEM TO
BE CONNECTED IN FINAL
CONFIGURATION FOR CALIB.

ATMOSPHERIC PRESSURE = p_a = 29.40 in Hg METER No. 4

	RUN 1							RUN 2						
R	C (ft^3)	time (sec)	P_m	P_1	Δp	t	P_2	C (ft^3)	time (sec)	P_m	P_1	Δp	t	P_2
10	0.2	130.0	0.1	3	0.008	80	1.8	0.2	127.0	0.1	3	0.008	80	1.9
30	0.8	129.3	0.6	12	0.139	80	10	0.8	134.5	0.6	12	0.133	80	10
50	1.5	133.3	1.5	30	0.479	80	27	1.4	125.6	1.6	31	0.458	80	27
70	2.1	124.0	3.1	62	1.025	80	58	2.1	122.2	3.2	65	1.043	80	60
85	2.7	139.5	5.0	95	1.575	80	89	2.7	135.0	5.0	96	1.576	80	90

R is rotameter reading C is ft^3 counted on dry gas meter for about 120 sec

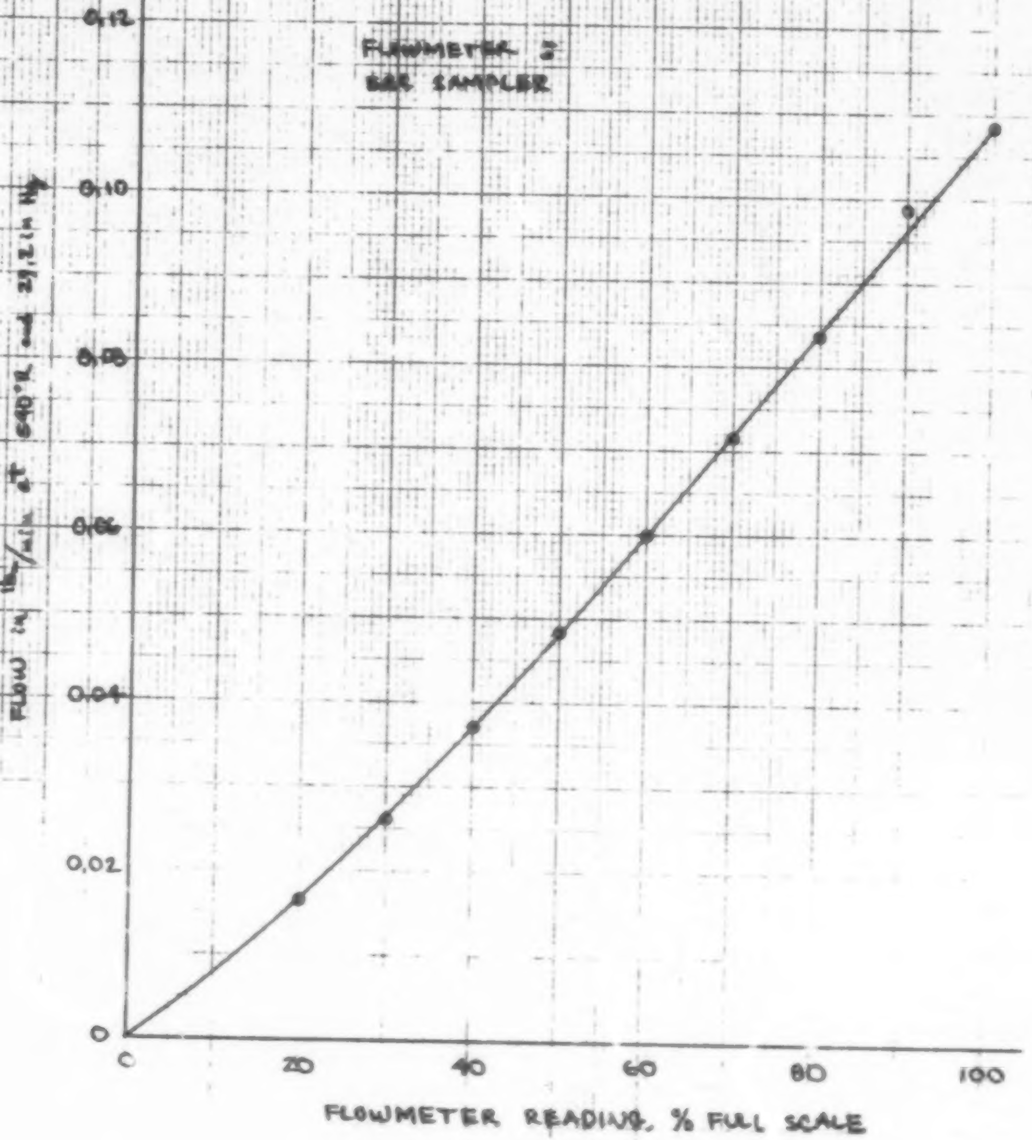
t is Temperature in °F P_m, P_1 & P_2 are in inches of H_2O

Δp is in inches of H_2O BY MICROMANOMETER $\rho_1 = 1.326\ P_1/T_1$

R	p_1	p_m	Δp	p_2	T	$\dot{m}$, lbm/min	Q, SCFM @ 70°F & 1 atm	Q DGM (corr.)
10	29.62	29.41	0.008	29.54	540	0.006 (0.00630)	0.08 (0.0841)	0.0901
30	30.28	29.44	0.136	30.14	540	0.0262	0.350	0.351
50	31.64	29.51	0.468	31.39	540	0.0498	0.665	0.651
70	34.07	29.63	1.034	33.74	540	0.0767	1.025	0.995
85	36.42	29.77	1.576	35.98	540	0.0979	1.308	1.153

Dry gas meter factor = 1.030

p_a, p_1 & p_2 are in inches of Hg absolute



11-3718-001
7/16/74
HARE

linearized: $\log_{10} \dot{M}_{300} = \log_{10} C + x \log_{10} \Delta P$

this computation can be performed in its entirety using STAT 1-24A using values from 3rd following page marked (x

$\log_{10} \Delta P_{ORIFICE}$	$\log_{10} \dot{M}_{300}$
− 0.7696	0.9694
− 0.6990	1.0726
− 0.3979	1.2263
− 0.2218	1.2951
− 0.0969	1.3591
0.00	1.4009
0.0792	1.4393
0.1461	1.4691
0.2041	1.4965
0.2553	1.5305
0.3010	1.5547
0.3979	1.6119
0.4771	1.6377
0.5441	1.6756
0.6021	1.7005
0.6532	1.7187
0.6990	1.7408
0.7404	1.7663
0.7782	1.7790
0.8129	1.8021
0.8451	1.8214

$n = 21$

$$\overline{(\log_{10} C)} = \overline{(\log_{10} \dot{M}_{300})} - x\,\overline{(\log_{10} \Delta P)}$$

$$x = \frac{n \sum_i (\log_{10}\Delta P)_i (\log_{10}\dot{M}_{300})_i - \sum_i (\log_{10}\Delta P)_i \sum_i (\log_{10}\dot{M}_{300})_i}{n \sum_i [(\log_{10}\Delta P)_i]^2 - \left(\sum_i (\log_{10}\Delta P)_i\right)^2}$$

	ALL POINTS (n=21)	HIGHEST 20 POINTS (n=20)
$\overline{(\log_{10} \Delta P)}$	= 0.2548	0.3060
$\overline{(\log_{10} \dot{M}_{300})}$	= 1.5274	1.5553
$\sum_i (\log_{10}\Delta P)_i$	= 5.3505	6.1201
$\sum_i (\log_{10}\dot{M}_{300})_i$	= 32.0755	31.1061
$\sum [(\log_{10}\Delta P)_i]^2$	= 6.0114	5.4191
$\sum_i (\log_{10}\Delta P)_i (\log_{10}\dot{M}_{300})_i$	= 10.4898	11.2359

ALL POINTS

$\therefore x = 0.5135$

$\overline{(\log_{10} C)} = 1.3966$

$\log_{10} \dot{M}_{300} = 1.3966 + 0.5135 \log_{10} \Delta P$

$\therefore \dot{M}_{300} = 24.92\ \Delta P^{0.5135}$

HIGHEST 20 POINTS

STAT 1-24A result

$\therefore x = 0.9842$

$x = 0.9842$

$\overline{(\log_{10} C)} = 1.4071$

$\log_{10} \dot{M}_{300} = 1.4071 + 0.9842 \log_{10} \Delta P$

$\therefore \dot{M}_{300} = 25.53\ \Delta P^{0.9842}$

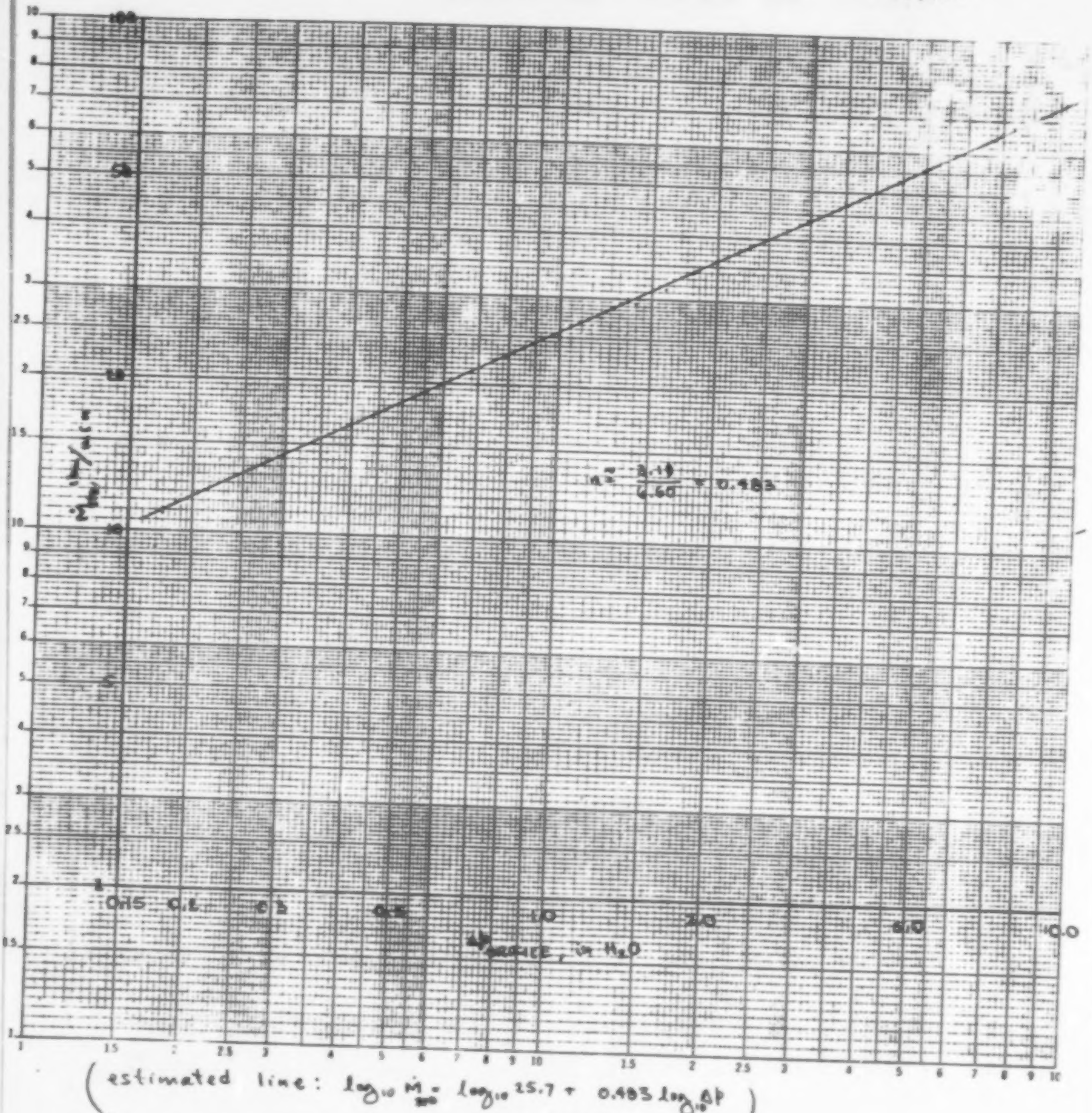
$\dot{M}_{300} = 25.54$

$\dot{m}_{0.18} = 10.19$ $\dot{m}_{10} = 77.85$

$\dot{M}_a = 89.60 (\Delta P\, \ell)^{0.9842}$

CALIBRATION OF ENGINE INLET
AIR ORIFICE

11-3718-001
4/9/71



(estimated line: $\log_{10}\dot{M}_{30} = \log_{10}25.7 + 0.483\log_{10}\Delta p$

$\therefore\ \dot{m}_{30} = 25.7(\Delta p)^{0.483}$)

actual line $\dot{m}_{30} = 25.53(\Delta p)^{0.4862}$

$\rho_{STD} = 0.07900$

11-3718-001
4/9/74

INLET AIR ORIFICE CALIBRATION

	RUN 1				RUN 2			
Δp ORIFICE	Q, UNCORR.	P CORR.	T CORR.	$\dot{M}_{STD}$ lbm/min	Q, UNCORR.	P CORR.	T CORR.	$\dot{M}_{STD}$ lbm/min
0.17	128.	0.9865	0.9642	9.11	131.	0.9840	0.9867	9.52
0.2	162.	0.9864	0.9737	11.65	165.	0.9839	0.9867	11.99
0.4	235.	0.9862	0.9737	16.89	232.	0.9837	0.9834	16.80
0.6	271.	0.9860	0.9737	19.48	276.	0.9835	0.9834	19.98
0.8	316.	0.9858	0.9737	22.71	318.	0.9833	0.9834	23.02
1.0	346.	0.9856	0.9802	25.02	351.	0.9832	0.9802	25.32
1.2	383.	0.9855	0.9770	27.60	380.	0.9830	0.9802	27.41
1.4	409.	0.9854	0.9737	29.38	408.	0.9829	0.9834	29.52
1.6	438.	0.9852	0.9727	31.45	434.	0.9827	0.9802	31.29
1.8	468.	0.9850	0.9737	33.60	475.	0.9826	0.9802	34.25
2.0	499.	0.9849	0.9705	35.70	500.	0.9824	0.9802	36.04
2.5	578.	0.9844	0.9642	41.07	566.	0.9820	0.9802	40.78
3.0	602.	0.9842	0.9642	42.76	612.	0.9817	0.9802	44.08
3.5	661.	0.9839	0.9674	47.10	664.	0.9813	0.9770	47.65
4.0	702.	0.9837	0.9674	50.01	704.	0.9812	0.9737	60.36
4.5	739.	0.9835	0.9674	62.63	728.	0.9810	0.9737	52.05
5.0	788.	0.9831	0.9705	56.28	779.	0.9806	0.9770	55.87
5.5	817.	0.9830	0.9705	58.34	812.	0.9806	0.9802	58.42
6.0	843.	0.9825	0.9705	60.17	849.	0.9801	0.9802	61.06
6.5	875.	0.9826	0.9705	62.45	898.	0.9800	0.9770	64.36
7.0	935.	0.9823	0.9674	66.51	925.	0.9795	0.9737	66.04

CALIBRATION OF ENGINE
INLET AIR ORIFICE

11-3718-001
4/9/74

⑦

ΔP ORIFICE	$\dot{M}_{STD}$, lbm/min AVG. 1 & 2
0.17	9.32
0.2	11.82
0.4	16.84
0.6	19.73
0.8	22.86
1.0	25.17
1.2	27.50
1.4	29.45
1.6	31.37
1.8	33.92
2.0	35.87
2.5	40.92
3.0	43.92
3.5	47.38
4.0	50.18
4.5	52.32
5.0	56.08
5.5	58.38
6.0	60.12
6.5	63.40
7.0	66.28

APPENDIX H

OPERATING INSTRUCTIONS AND THEIR DEVELOPMENT

11-3718-001
7/21/74

ERC SAMPLER INSTRUCTIONS

INITIAL: PUMPS ON – DUMMY FILTER – SET FLOWMETER 5 AT 70

1. ESTABLISH ENGINE OPERATING CONDITION WITH EXHAUST BACKPRESSURE BETWEEN 0.5 AND 2.0 in Hg (IF POSSIBLE) –
   – IDLE BACKPRESSURE SHOULD BE ABOUT 0.5, OTHERS 1.0 OR MINIMUM, WHICHEVER IS LARGER

2. CALCULATE EXHAUST MASS FLOW = $\dot{M}_e = \dot{M}_a$ (AIR) + $\dot{M}_f$ (FUEL)

   READ $\dot{M}_f$ from FLO-TRON ; $\dot{M}_a = 89.60(\Delta p_E \rho_E)^{0.4842} = 527.1\left(\frac{\Delta p_E}{T+460}\right)^{0.4842}$,
   OR READ $\dot{M}_a$ from ERC GRAPH 0
   – IN THE $\dot{M}_a$ EQUATION: "Δp_E" IS ENGINE AIR ORIFICE; "T" IS ENGINE AIR INLET TEMP (① ON ENGINE OPERATOR'S DIGITAL READOUT)

3. CALCULATE RAW SAMPLE $\Delta p = \Delta p_v = (9.90 \times 10^{-4})\dot{M}_e^{1.86}$ OR
   READ Δp_v from ERC GRAPH 1

4. SET DILUTE SAMPLE FLOW RATE AT 50 ACFM USING
   ERC GRAPH 2 AT T_{ds} (④ ON TUNNEL DIGITAL READOUT)

5. CALCULATE PRIMARY DILUTION $\Delta p = \Delta P_{da} = (1.94 \times 10^{-6}) \frac{T_E^{4/3}}{T_{da}^{1/3}} \dot{M}_e^2$ OR
   READ Δp_{da} from ERC GRAPH 3

6. SET Δp_v AND Δp_{da} USING SHUTTER AND DILUTION AIR CONTROL

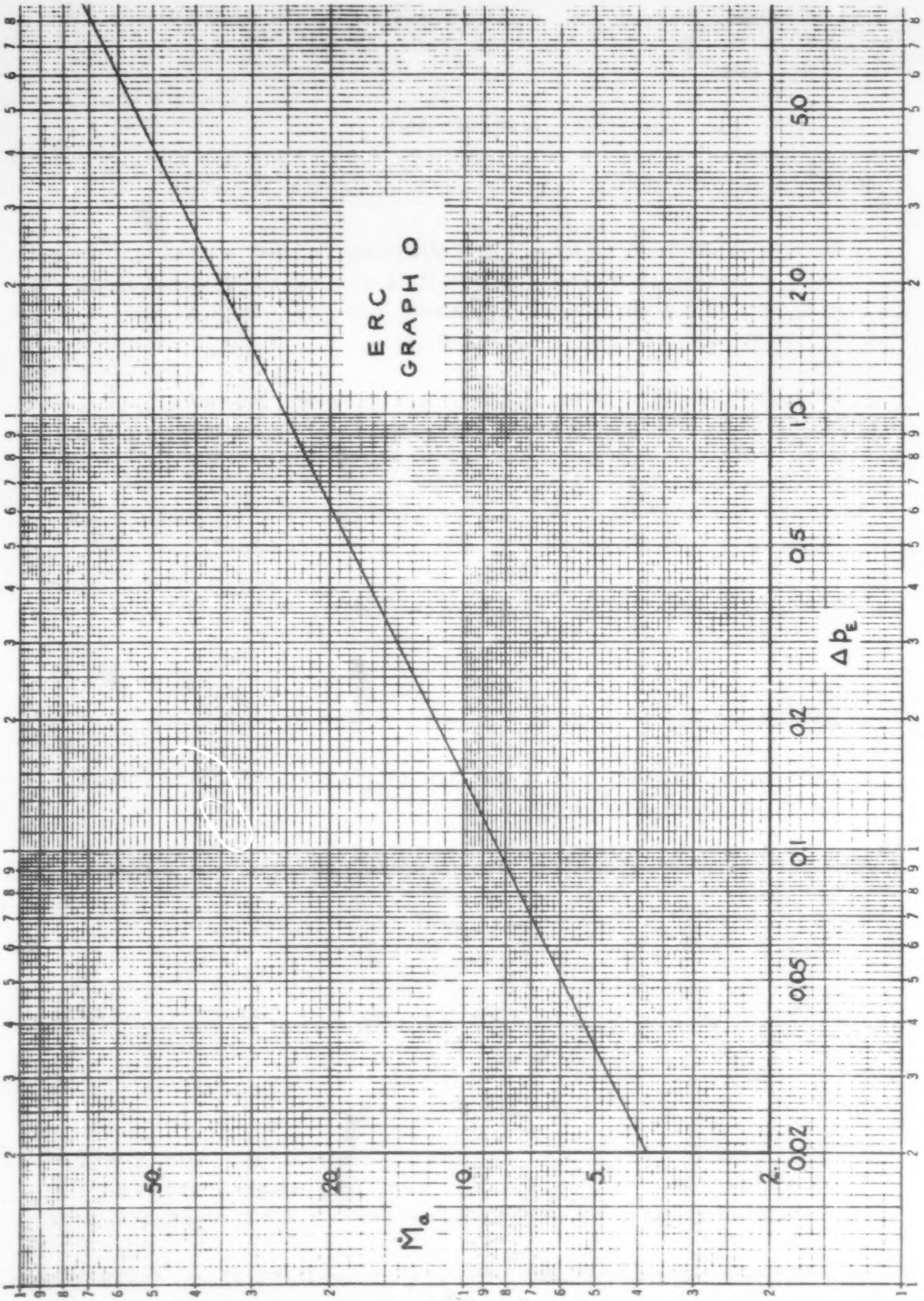
7. CALCULATE RAW SAMPLE FLOW RATE = $\dot{m}_s = 0.00186\,\dot{M}_e$ OR
   READ $\dot{m}_s$ from ERC GRAPH 4

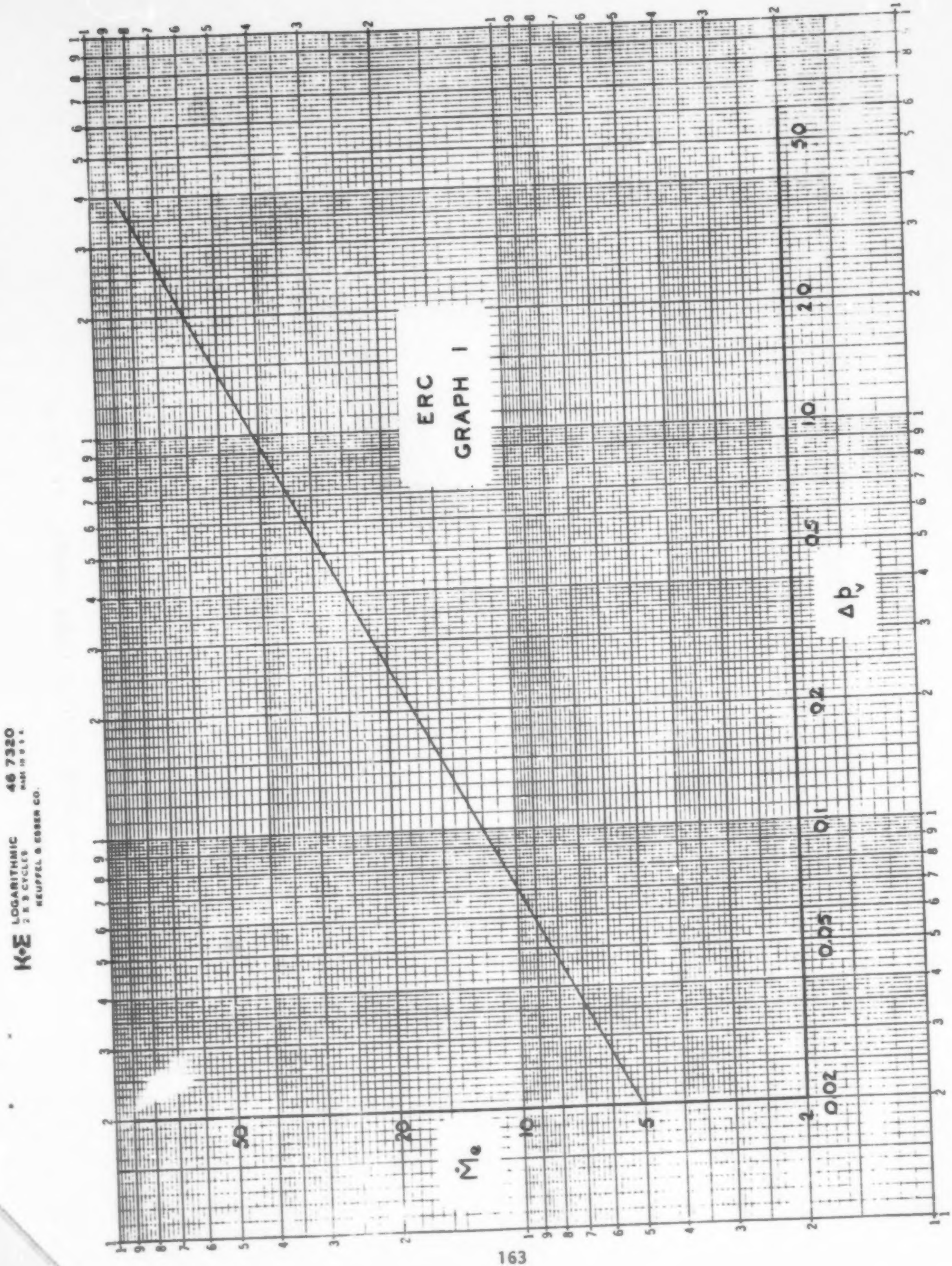
8. TURN OFF 1 CFM SAMPLE PUMP AND INSTALL CORRECT FLUOROPORE FILTER

9. RECORD DRY GAS METER READING

10. SIMULTANEOUSLY START 1 CFM SAMPLE PUMP AND TIMER; RESET No. 5 FLOWMETER $(1\,ACFM)_{ds}$ AND No. 5 CALIBRATION CURVE; AND RECORD DATA AT INDICATED INTERVALS ON SAMPLER OP'S. SHEET

11. SHUT DOWN 1 CFM PUMP AND TIMER WHEN INDICATED OR IF FILTER PLUGS


ERC
GRAPH O
Δp_E
0.02
0.05
0.1
0.2
0.5
1.0
2.0
5.0
Ṁ_a
2
5
10
20
50


K+E LOGARITHMIC 2 X 3 CYCLES KEUFFEL & ESSER CO.
46 7320 MADE IN U.S.A.
ERC
GRAPH 1
Δp_v
0.02
0.05
0.1
0.2
0.5
1.0
2.0
5.0
$\dot{M}_e$
2
5
10
20
50

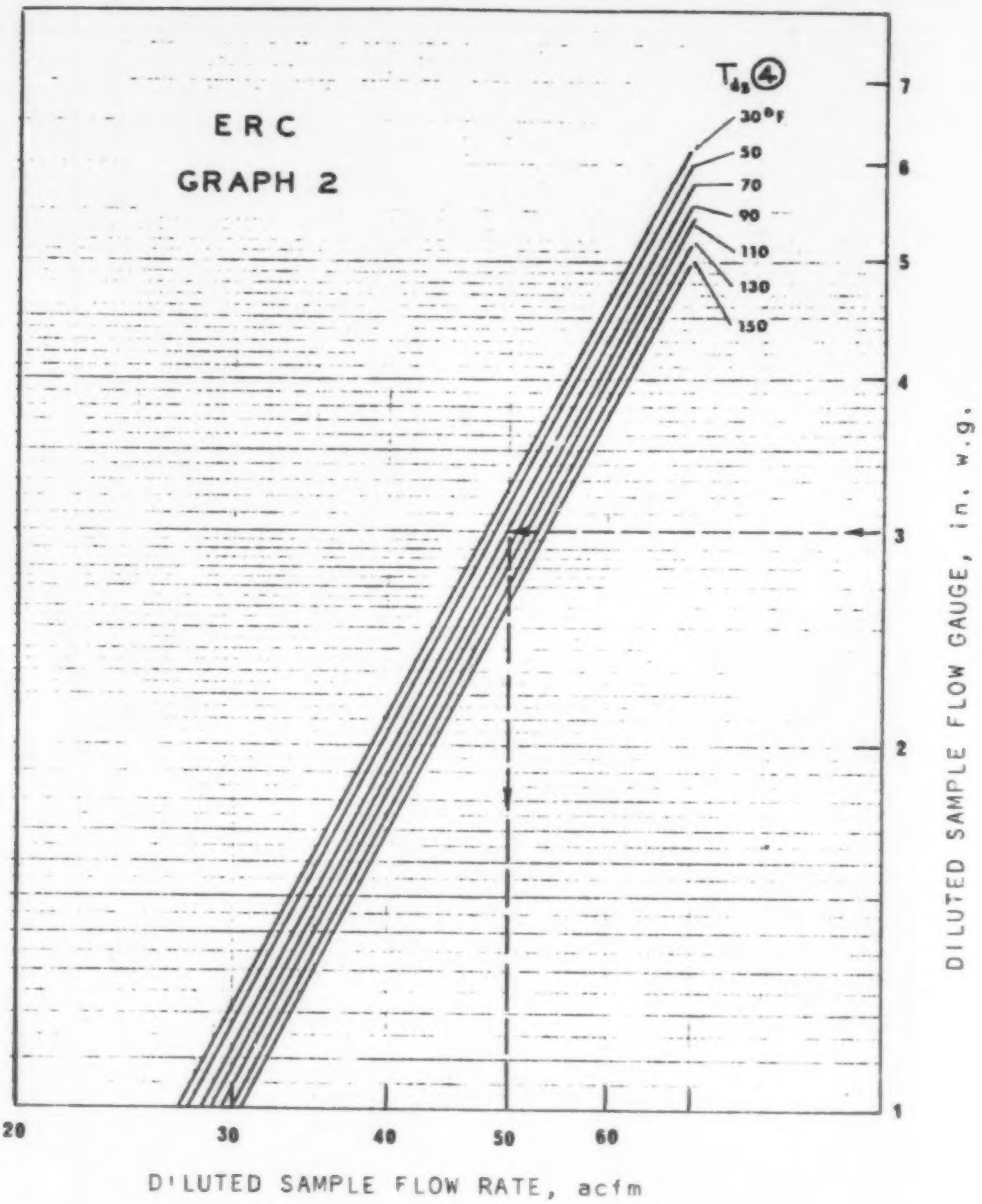
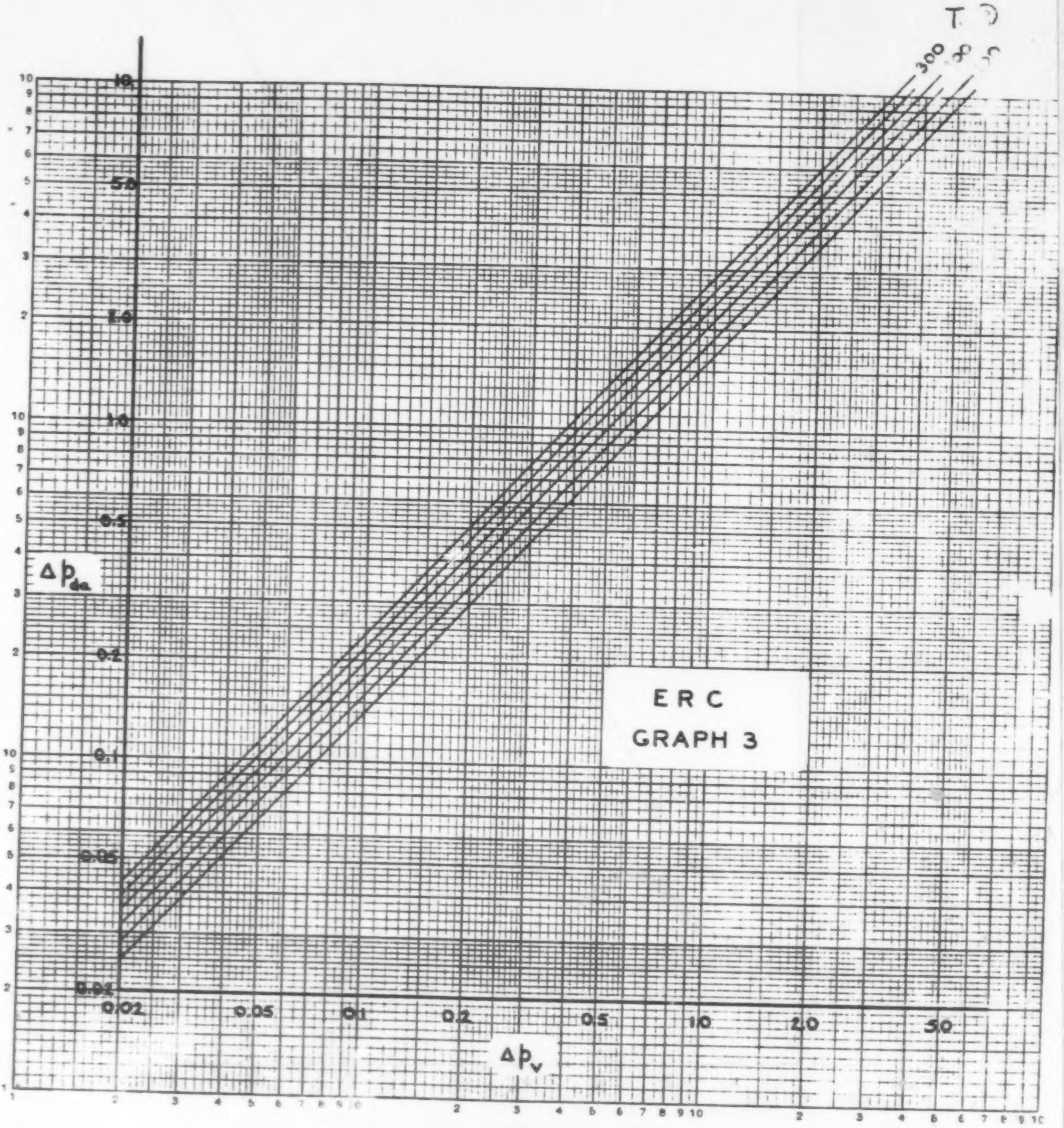
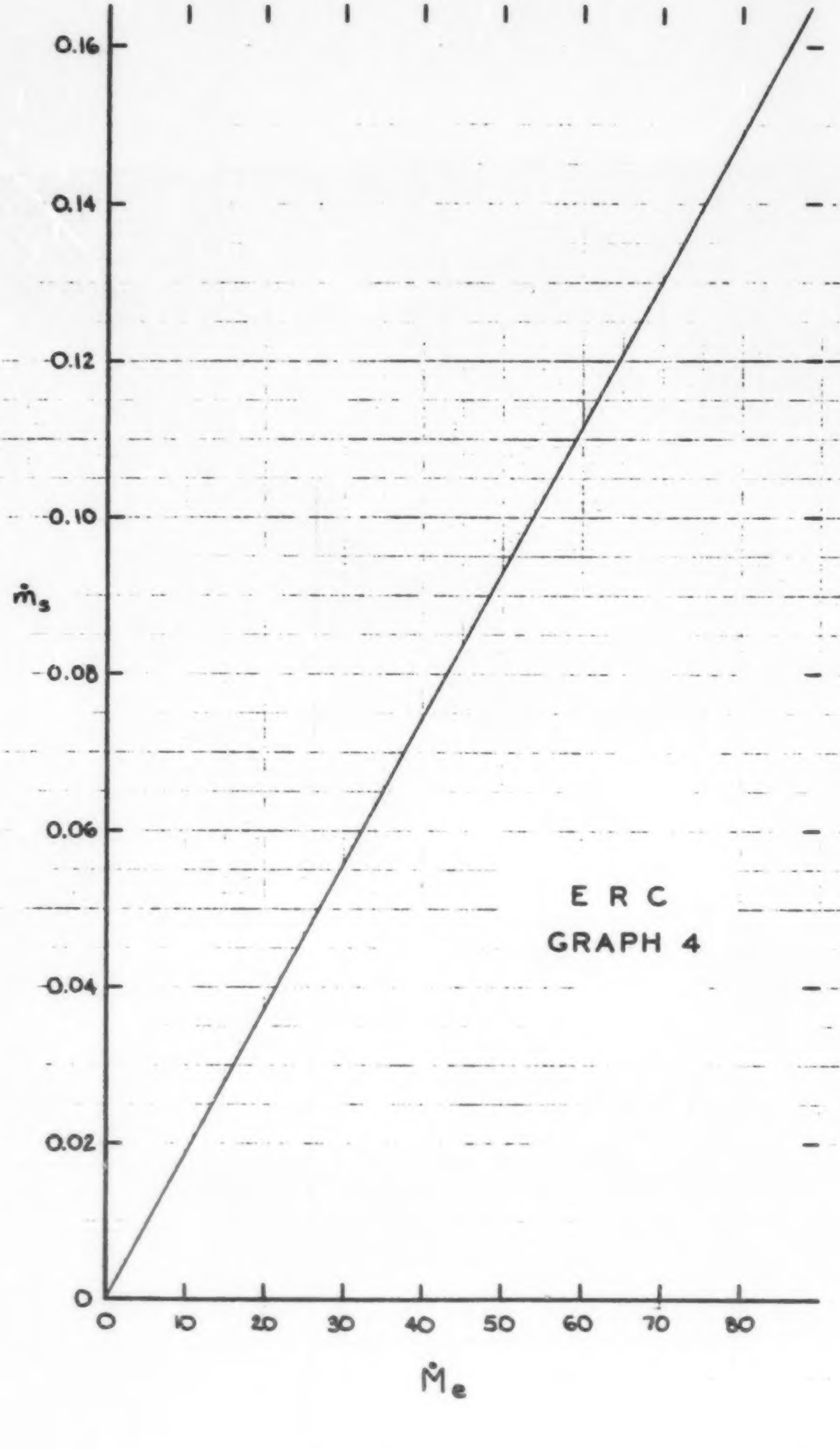


Figure 15. Diagram of the Diluted Sample Flow Rate



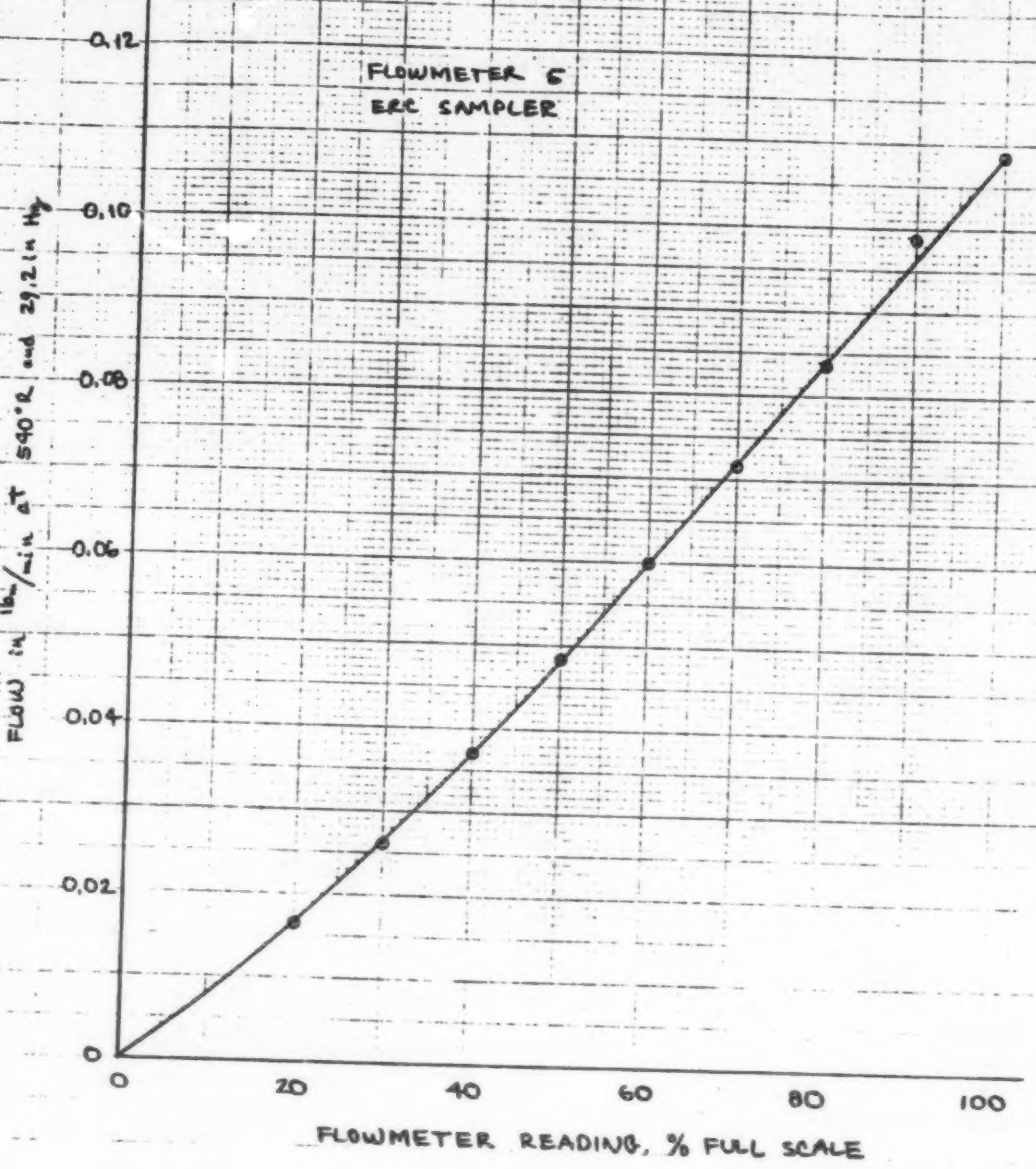
ERC
GRAPH 3

T
300
Δp_{da}
10
5.0
2.0
1.0
0.5
0.2
0.1
0.05
0.02
0.02
0.05
0.1
0.2
0.5
1.0
2.0
5.0
Δp_v



0.16
0.14
0.12
0.10
$\dot{m}_s$
0.08
0.06
0.04
0.02
0
0
10
20
30
40
50
60
70
80
$\dot{M}_e$

E R C
GRAPH 4



11-3718-001
7/16/74
HARE

11-3718-001
7/16/74

SAMPLING RATE DATA & CALCULATIONS

PROBE		TIP		
LOCATION	No.	I.D., in	AREA, in²	AREA, ft²
HI-VOL (8×10)	—	3.47 (derived)	9.46	0.0657
4×47 unit	1	0.500	0.196	0.00136
	2	0.500	0.196	0.00136
	3	0.501	0.197	0.00137
	4	0.501	0.197	0.00137
ERC sampler	2	0.2535	0.0505	0.000350
	3	0.2005	0.0316	0.000219
	4	0.3035	0.0723	0.000502
	5	0.1510	0.0179	0.000124
	6	0.1005	0.00793	0.0000551

TUNNEL CALIBRATION

$$V_{sb} = N \frac{\text{counts}}{\text{time}}\left(\frac{T_s}{T_2}\times\frac{P_2}{P_s}\right)$$ at blower Δp of 3.5 in H_2O

N = 11.9 for 4×47 system, 12.4 for HI-VOL system

ISOKINETIC SPEEDS

$$\text{HI-VOL: } V_{iso} \doteq 1.11\ V_{sb} = \frac{Q_s\,(\text{sample})}{A_s\,(\text{sample})} = \frac{\dot{m}/\rho_s}{A_s\,(\text{sample})} = \frac{278.9\sqrt{\rho_{OR}\Delta P_{OR}}}{\rho_s A_s\,(\text{sample})}\ \text{ft/hr}$$

$$= \frac{4.648\sqrt{\rho_{OR}\Delta P_{OR}}}{\rho_s A_s\,(\text{sample})} = \frac{70.76\sqrt{\rho_{OR}\Delta P_{OR}}}{\rho_s}\ \text{ft/min}$$

$$\therefore V_{sb} = \frac{63.75\sqrt{\rho_{OR}\Delta P_{OR}}}{\rho_s}\ \text{ft/min} \qquad \therefore \Delta P_{OR} \text{ for isokinetic flow} = \frac{\rho_s^2 V_{sb}^2}{4064\ \rho_{OR}}$$

4×47mm SYSTEM: $V_{iso} = 1.11\ V_{sb}$; $\dot{m} = 1.11 V_{sb}\,\rho_s\,a_s\,(\text{sample})$

let $\dot{m} = (x)\,V_{sb}\,\rho_s$ lbm/min

PROBE No.	TIP I.D., in	(x)
1	0.500	0.00151
2	0.500	0.00151
3	0.501	0.00152
4	0.501	0.00152

ERC SAMPLER

ISOKINETIC RATE = 1.1 ($^{a}/_{A}$) EXH. FLOW ($^{lbm}/_{min}$)

VENTURI Δp_v for ISOKINETIC FLOW

$p_a = 29.3$: $\Delta p_v = (9.90 \times 10^{-4}) \dot{M}_e^{1.86}$

p_a = variable: $\Delta p_v = \dfrac{(0.0289)\dot{M}_e^{1.86}}{p_a}$

} Calculations on next page

Probe No.	Tip I.D., in	(1.1 $^{a}/_{A}$)
2	0.2535	0.00297
3	0.2005	0.00186
4	0.3035	0.00426
5	0.1510	0.00106
6	0.1005	0.000467

ENGINE AIR FLOW RATE = $\dot{M}_a = 89.60\,(\Delta p\,\rho)^{0.4842}$; $\dot{M}_e = \dot{M}_a + \dot{M}_f$

for $p_a = 29.3$, $\dot{M}_a = 527.1\,(^{\Delta p}/_{T})^{0.4842}$, error < 0.5% for $29.0 \le p_a \le 29.6$

for T = 70F, $\dot{M}_a = 25.28\,(\Delta p)^{0.4842}$, error < 1% for 60F ≤ T ≤ 80F

	DRY GAS METER FACTORS				
No	1	2	3	4	*5
FACTOR	1.027	1.046	1.035	1.030	1.0

* this unit used on ERC sampler

11-3718-001
7/17/74

EXTRAPOLATION OF VENTURI CURVES - ERC

DATA $T_v = 100F$ $P_a \equiv 29.3$ in Hg $\therefore \rho \equiv 0.0694$ Q in ACFM, $\dot{m}$ in lb-/min

Δp	1	2	4	8	10
Q	(1.118) 1.11	1.64	2.39	3.46	(3.909) 3.89
$\dot{m}$	(0.0776) 0.0770	0.114	0.166	0.240	(0.2714) 0.270

$Q = a(\Delta p)^b$ $\dot{m} = c(\Delta p)^d$
$a = 1.118$ $c = 0.07761$
$b = 0.5438$ $d = 0.5436$
$r^2 = 0.9999$ $r^2 = 0.9998$

DATA $T_v = 200F$ $P_a \equiv 29.3$ in Hg $\therefore \rho \equiv 0.0589$

Δp	1	2	4	8	10
Q	(1.233) 1.22	1.81	2.62	3.77	(4.258) 4.23
$\dot{m}$	(0.0740) 0.0718	0.112	0.154	0.222	(0.2510) 0.249

$Q = a(\Delta p)^b$ $\dot{m} = c(\Delta p)^d$
$a = 1.233$ $c = 0.07405$
$b = 0.5382$ $d = 0.5302$
$r^2 = 0.9997$ $r^2 = 0.9969$

DATA $T_v = 300F$ $P_a \equiv 29.3$ in Hg $\therefore \rho \equiv 0.0511$

Δp	1	2	4	8	10
Q	(1.336) 1.32	1.96	2.83	4.07	(4.588) 4.55
$\dot{m}$	(0.0785) 0.0777	0.115	0.167	0.240	(0.2705) 0.268

$Q = a(\Delta p)^b$ $\dot{m} = c(\Delta p)^d$
$a = 1.336$ $c = 0.07852$
$b = 0.5360$ $d = 0.5371$
$r^2 = 0.9996$ $r^2 = 0.9996$

ALL 15 POINTS $\dot{m} = c(\Delta p)^d$ $(\Delta p)_1 = 0.0767$
$c = 0.07670$ $(\Delta p)_{10} = 0.2641$
$d = 0.5370$
$r^2 = 0.9942$

about 27.1% from
29.0 ≤ P_a ≤ 29.6

$\therefore \underline{\underline{\dot{m} = 0.0767(\Delta p)^{0.537}}}$ at 29.3 in Hg, $100 \le T_v \le 300$

for variable P_a: $\underline{\underline{\dot{m} = 0.0767\left(\frac{\Delta p \, P_a}{29.3}\right)^{0.537}}}$

for isokinetic flow, $P_a = 29.3$, probe tip I.D. = 0.2005 in

$$\Delta p = (13.04\ \dot{m})^{1.86} = (0.02425\ \dot{M}_e)^{1.86} = (9.90 \times 10^{-4})\ \dot{M}_e^{1.86}$$

for isokinetic flow, variable P_a, probe tip I.D = 0.2005 in

$$\Delta p = \frac{(79.95\ \dot{m})^{1.86}}{P_a} = \frac{(0.1485\ \dot{M}_e)^{1.86}}{P_a} = \frac{(0.0289)\dot{M}_e^{1.86}}{P_a}$$

7/10/74

CALCULATION OF Δp_{da} IN TERMS OF KNOWN QUANTITIES

BASIC EQ: $\Delta p_{da}(\text{psi}) = 1.3\,\rho_{da}\dfrac{V_{da}^2}{2g}$; ρ in $\frac{\text{lb}_m}{\text{ft}^3}$; V in $\frac{\text{ft}}{\text{sec}}$; $g = 32.2\,\frac{\text{ft lb}_m}{\text{lb}_f\,\text{sec}^2}$

$$\Delta p_{da}(\text{in } H_2O) = 1.3\,\rho_{da}\frac{V_{da}^2}{2g} \times \frac{g\ \text{lb}_f\,\text{sec}^2}{32.2\ \text{ft lb}_m} \times \frac{27.69\ \text{in } H_2O}{1\ \text{psi}} = 0.559\,\rho_{da}(V_{da})^2$$

check: $\rho_{da} = 0.07$, $V_{da} = 6.25$; $\Delta p_{da} = 1.52$ in H_2O ✓ (reasonable)

$V = Q/A$ $\therefore$ $\Delta p_{da} = 0.559\,\rho_{da}\left(\frac{Q_{da}}{A}\right)^2$; Q in $\frac{\text{lb}_m}{\text{sec}}$; A in $\text{ft}^2 = A_{da} = A_s = 0.00267\ \text{ft}^2$

to get Q to $\frac{\text{lb}_m}{\text{min}}$: $\Delta p_{da} = 0.559\,\rho_{da}\left(\frac{Q_{da}}{A}\right)^2\left(\frac{1\ \text{min}}{60\ \text{sec}}\right)^2 = (1.55\times10^{-4})\,\rho_{da}\left(\frac{Q_{da}}{A}\right)^2$

FOR $KE_{da} = KE_s$: $\rho_s Q_s V_s^2 = \rho_{da} Q_{da} V_{da}^2$; $V = Q/A$; $A_{da} = A_s$

$$\therefore \rho_s Q_s^3 = \rho_{da} Q_{da}^3 \quad \therefore Q_{da} = Q_s\left(\rho_s/\rho_{da}\right)^{1/3}$$

$$\therefore \Delta p_{da} = (1.55\times10^{-4})\,\rho_{da}\frac{Q_s^2\,\rho_s^{2/3}}{A^2\,\rho_{da}^{2/3}} \ ; \quad Q_s = \dot{m}_s/\rho_s$$

$$\therefore \Delta p_{da} = (1.55\times10^{-4})\frac{\rho_{da}^{1/3}}{\rho_s^{4/3}}\frac{\dot{m}_s^2}{A^2} = (21.74)\frac{(\rho_{da})^{1/3}}{(\rho_s)^{4/3}}\dot{m}_s^2$$

FOR $\rho = 1.326\,\frac{p}{T}$, p in in Hg, T in °R ; assume $p_s = p_{da} = p_a$

$$\therefore \underline{\underline{\Delta p_{da}}} = (21.74)\frac{\left(1.326\frac{p_a}{T_{da}}\right)^{1/3}}{\left(1.326\frac{p_a}{T_s}\right)^{4/3}}(\dot{m}_s^2) = \underline{\underline{(16.40)\frac{(T_s)^{4/3}}{p_a(T_{da})^{1/3}}(\dot{m}_s)^2}}$$

FOR $p_a = 29.3$

$$\underline{\underline{\Delta p_{da} = (0.560)\frac{(T_s)^{4/3}}{(T_{da})^{1/3}}(\dot{m}_s)^2}}$$

FURTHER: $\dot{m}_s = 0.00186\ \dot{M}_e$ for 0.2005 in I.D. sampling nozzle

$$\therefore \underline{\underline{\Delta p_{da}}} = (16.40)\frac{(p_a/T_{da})^{1/3}}{(p_a/T_s)^{4/3}}(0.00186\,\dot{M}_e)^2 = \underline{\underline{(5.67\times10^{-5})\frac{(p_a/T_{da})^{1/3}}{(p_a/T_s)^{4/3}}\dot{M}_e^2}}$$

FOR $p_a = 29.3$; $\underline{\underline{\Delta p_{da} = (1.94\times10^{-6})\frac{(T_s)^{4/3}}{(T_{da})^{1/3}}\dot{M}_e^2}}$

NOTE: T_s USED HERE
IS T_v ② ON
DATA SHEETS

NOTE: T_s USED HERE
IS T_v ② ON
DATA SHEETS

11-3718-001
7/19/74

TO GENERATE Δp_{da} vs Δp_v CURVES: p_a, T_s, T_{da} AS PARAMETERS

$p_a = 29.3$: $\Delta p_{da} = (1.94 \times 10^{-6}) \dfrac{T_s^{4/3}}{T_{da}^{1/3}} \dot{M}_e^2$ $\qquad \Delta p_v = (0.02425\, \dot{M}_e)^{1.86} = (9.90 \times 10^{-4}) \dot{M}_e^{1.86}$

$\therefore \dot{M}_e = 41.24 (\Delta p_v)^{0.537}$ $\qquad \therefore \Delta p_{da} = (3.30 \times 10^{-3}) \dfrac{T_s^{4/3}}{T_{da}^{1/3}} (\Delta p_v)^{1.074}$

$T_{da} = 530\,R$ (70F) $\qquad \therefore \Delta p_{da} = (4.08 \times 10^{-4})\, T_s^{4/3} (\Delta p_v)^{1.074} = K (\Delta p_v)^{1.076}$

T_s	K	$\Delta p_{da}\vert_{\Delta p_v = 0.2}$	$\Delta p_{da}\vert_{\Delta p_v = 1}$	$\Delta p_{da}\vert_{\Delta p_v = 3}$
510	1.662	0.295	1.662	5.41
560	1.882	0.334	1.882	6.12
610	2.110	0.375	2.110	6.87
660	2.343	0.416	2.343	7.62
710	2.583	0.459	2.583	8.41
760	2.828	0.502	2.828	9.20

$T_{da} = 540\,R$ (80F) $\qquad \therefore \Delta p_{da} = (4.05 \times 10^{-4})\, T_s^{4/3} (\Delta p_v)^{1.074} = K (\Delta p_v)^{1.074}$

T_s	K
510	1.651
560	1.871
610	2.096
660	2.329
710	2.567
760	2.811

$T_{da} = 550\,R$ (90F) $\qquad \therefore \Delta p_{da} = (4.03 \times 10^{-4})\, T_s^{4/3} (\Delta p_v)^{1.074} = K (\Delta p_v)^{1.074}$

T_s	K
510	1.641
560	1.859
610	2.084
660	2.314
710	2.551
760	2.793

IS T_v ② ON DATA SHEETS

11-3718-001
7/19/74

$P_a = 29.3$ (cont'd).

$T_{da} = 520$ R (60F) $\quad \therefore \Delta p_{da} = (4.10 \times 10^{-4})\, T_s^{4/3} (\Delta p_v)^{1.074} = K (\Delta p_v)^{1.074}$

T_s	K
510	1.672
560	1.894
610	2.123
660	2.358
710	2.599
760	2.846

$p_a = 29.2$: $\quad \Delta p_{da} = (1.94 \times 10^{-6}) \dfrac{T_s^{4/3}}{T_{da}^{1/3}} \dot{M}_a^2 \qquad \Delta p_v = (9.90 \times 10^{-4})\, \dot{M}^{1.86}$

NO CHANGE (ROUNDING ERROR ONLY, < 0.1%)

SO — USE FIGURES FOR 70F (WITHIN 1% $60F \leq T_{da} \leq 80F$) AND 29.3 in Hg (WITHIN 1% $29.0 \leq p_a \leq 29.6$)

NOTE: T_s USED HERE
IS T_v ② ON DATA
SHEETS

11-3718-001
7/19/74

VERIFICATION OF Δp_v vs Δp_{da} RELATIONSHIP

METHOD: CHOOSE T_s & T_{da} EQUAL, THEN $\rho_s = \rho_{da}$ AND $V_s = V_{da}$, etc.

$Q_s = Q_{da} = 1.0$ CFM $\quad V_s = V_{da} = 6.24$ ft/sec $\quad \rho_{da} = 0.0733 \frac{lbm}{ft^3}$ @ 29.3 & 70F

$\Delta p_{da} = 0.559\, \rho_{da}(V_{da})^2$ from ERC manual (Δp – in H_2O, ρ – lbm/ft³, V – ft/sec)

$\therefore \Delta p_{da} = 1.596$ in H_2O

from my equations: $\Delta p_v = (13.04\, \dot{m})^{1.86} = (13.04 \times 0.0733)^{1.86} = 0.919$ in H_2O

from my graph: $\Delta p_{da} \cong 1.58$ in H_2O — VERIFIED

$Q_s = Q_{da} = 2.0$ CFM $\quad V_s = V_{da} = 12.5$ ft/sec $\quad \rho_{da} = 0.0733 \frac{lbm}{ft^3}$ @ 29.3 & 70F

$\Delta p_{da} = 0.559\, \rho_{da}(V_{da})^2 = 6.402$ in H_2O

$\Delta p_v = (13.04\, \dot{m})^{1.86} = (13.04 \times 0.147)^{1.86} = 3.35$ in H_2O

from my graph: $\Delta p_{da} \cong 6.35$ in H_2O – VERIFIED

7/22/74

GENERAL CONDITIONS AND LIMITS

1. $29.0 \text{ in Hg} \le p_a \le 29.6 \text{ in Hg}$

2. raw sample temperature ② $50F \le T_v \le 300 F$

3. ERC dilution air temperature ③ $60F \le T_{da} \le 80F$

4. ERC sampling nozzle I.D. = 0.2005 in

5. EXHAUST PIPE I.D. (upstream of muffler) = 4.875 in

6. ERC SAMPLE LINE CONFIGURATION — 50 inch line 0.5 inch O.D. SS; 6 inch line 0.25 inch O.D. SS; 30 inch standard ERC sample line

11-3718-001
7/22/74

DILUTION TUNNEL OPERATING INSTRUCTIONS

A. HI-VOL (8X10 FILTER) SYSTEM

1. SET Δp_{OR} (ORIFICE IN TAILPIPE) = 2.05 in H_2O WITH ENGINE OFF AND DILUTION TUNNEL BLOWER ON — SWITCH OFF SAMPLE BLOWER

2. START ENGINE AND ESTABLISH OPERATING CONDITION AS QUICKLY AS POSSIBLE

3. START SAMPLE BLOWER, COUNTER, & TIMER SIMULTANEOUSLY; CORRECT Δp_{OR} AS NECESSARY DURING RUN USING SPEED CONTROL

4. STOP SAMPLE BLOWER, COUNTER, & TIMER SIMULTANEOUSLY AT END OF RUN

B. 4×47 mm SYSTEM

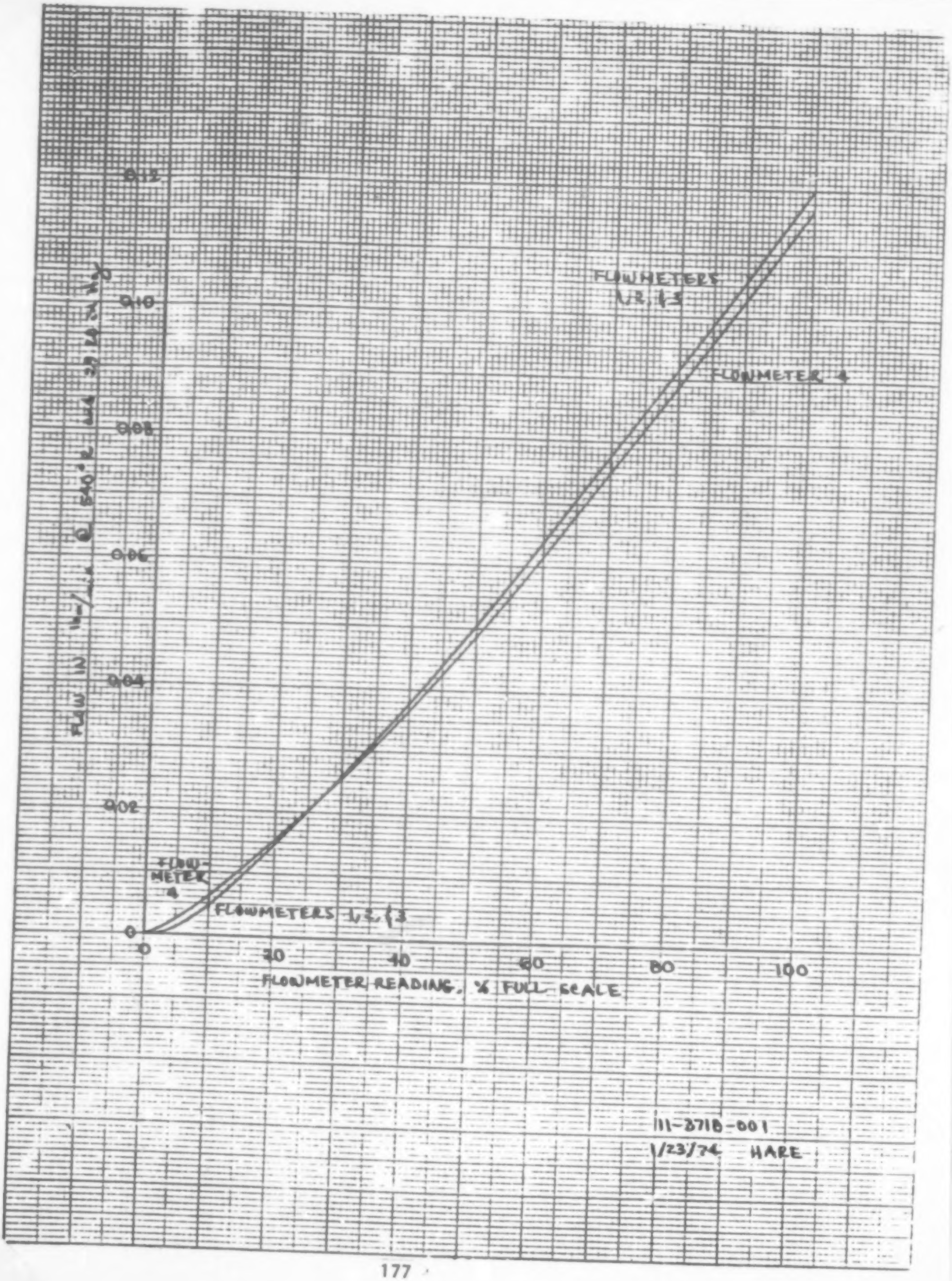
1. SET FLOWMETERS WITH ENGINE OFF AS FOLLOWS, USING CALIBRATION CURVES FOR METERS 1 — 4 (TUNNEL BLOWER ON):

$$\left.\begin{array}{l} \text{FLOWMETERS 1 \& 2: } \dot{m} = 19.2/(T_s+460) \\ \text{" \quad " 3 \& 4: } \dot{m} = 19.3/(T_s+460) \end{array}\right\} \text{TO NEAREST 1\% OF SCALE}$$

2. STOP PUMPS AND TAKE "BEFORE" DRY GAS METER READINGS, THEN START ENGINE AND ESTABLISH CONDITION AS QUICKLY AS POSSIBLE

3. START PUMPS, COUNTER, & TIMER SIMULTANEOUSLY; CORRECT FLOWMETER READINGS AS NECESSARY DURING RUN USING VALVES

4. STOP PUMPS, COUNTER, & TIMER SIMULTANEOUSLY AT END OF RUN



111-3718-001
1/23/74 HARE

APPENDIX I

PROCEDURES FOR DATA REDUCTION

SAMPLER OPERATOR ____________________ DATE __/__/__ RUN ______

FOR MULTIMODE RUNS

	TIME (sec) AT		ENGINE		TEMP'S., °F				Δp, in H_2O			FLOWMETER R.					ORIFICE
MODE	START	END	RPM	LOAD, %	T_p ①	T_v ②	T_{DA} ③	T_{DS} ④	PRIM. DIL.	RAW S. (VENTURI)	DIL. SAMPLE	1	2	3	4	5	Δp
1																	
2																	
3																	
4																	
5																	
6																	
7																	
8																	
9																	
10																	
11																	
12																	
13																	

FOR SINGLE-MODE RUNS (STEADY-STATE)

RPM= ______ %LOAD= ______ LOAD(lb_f)= ______

	TIME, sec	TIME, min	TEMP'S., °F				Δp, in H_2O			FLOWMETER R.					ORIFICE
			T_p ①	T_v ②	T_{DA} ③	T_{DS} ④	PRIM. DIL.	RAW S. (VENTURI)	DIL. SAMPLE	1	2	3	4	5	Δp
1															
2															
3															
4															
5															
6															
7															
8															
9															
10															
11															
12															
13															

FILTER No. BY POSITION	
1	FP47-
2	A47-
3	A47-
4	A47-
5	FP47-
R	AR-

	DRY GAS METER	
	BEFORE	AFTER
1		
2		
3		
4		
5		

ENGINE ______________________ ERC PROBE TIP I.D. ______

TUNNEL OPERATOR ______________ DATE _/_/_ RUN ___

FOR MULTIMODE RUNS

	TIME (sec) AT		ENGINE		TEMP'S., °F					BLOWER		VALVE TURNS CLO.		NO_x RAW		NO_x DILUTE	
MODE	START	END	RPM	LOAD, %	T_A ⑧	T_S ⑨	T_F ⑩	T_{DB} ⑪	T_B ⑫	Δp	P_s	LARGE	SMALL	RANGE	CHART	RANGE	CHART
1																	
2																	
3																	
4																	
5																	
6																	
7																	
8																	
9																	
10																	
11																	
12																	
13																	

FOR SINGLE-MODE RUNS (STEADY-STATE)

RPM = ______ % LOAD = _____ LOAD (lb_f) = ______

TUNNEL BLOWER COUNTS					
SAMPLING TIME, sec					

	TIME,	TIME,	TEMP'S., °F					BLOWER		VALVE TURNS CLO.		NO_x RAW		NO_x DILUTE	
	sec	min	T_A ⑧	T_S ⑨	T_F ⑩	T_{DB} ⑪	T_B ⑫	Δp	P_s	LARGE	SMALL	RANGE	CHART	RANGE	CHART
1															
2															
3															
4															
5															
6															
7															
8															
9															
10															
11															
12															

ENGINE ______________ FILTER(S) ______________

FOR MULTIMODE RUNS

	TIME(sec) AT		ENGINE			INTAKE AIR		RESTRICTIONS		FUEL,
MODE	START	END	RPM	LOAD, %	LOAD, lb_f	ΔP_E, in H_2O	T_E, °F	INTAKE, in H_2O	EXHAUST, in Hg	lb_m/hr
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										

FOR SINGLE-MODE RUNS (STEADY-STATE)

RPM = ______ %LOAD = ______ LOAD(lb_f) = ________

	TIME,	TIME,	INTAKE AIR		RESTRICTIONS		FUEL,
	sec.	min	ΔP_E, in H_2O	T_E, °F	INTAKE, in H_2O	EXHAUST, in Hg	lb_m/hr
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							

ENGINE ______________________ FUEL __________ p_B = _____ in Hg

WET BULB = ____ °F DRY BULB = ____ °F EXH. SYSTEM ______________

FILTER(S) ________________

11-3718-001
8/13/74

DATA REDUCTION PROCEDURES

DATA

ONE VALUE PER TEST

wt. of particulate in g = G_{AR}, G_{47j}, G_{ERC}
total sampling time = (time) = $\sum(\text{time})_i$, sec
blower counts = C_B
blower rate in counts/sec = R = $C_B/(\text{time})$
atmospheric pressure = p_a (in Hg)
initial dry gas meter readings = V_{1j}, ft^3
final " = V_{2j}, ft^3
number of modes = N

ONE VALUE PER MODE

raw NO_x concentration = $(NO_x)_R$, ppm
dilute NO_x concentration = $(NO_x)_D$, ppm
engine air orifice Δp = Δp_E, in H_2O
engine air temperature = T_E, °F
blower inlet temperature = T_B, °F
time in mode = $(\text{time})_i$, sec
engine fuel rate = $\dot{M}_f$, lbm/hr
hi-vol orifice Δp = Δp_{OR}, in H_2O
hi-vol orifice temperature = T_{OR}, °F

EQUATIONS

$$\rho_E \cong 1.326\, p_a/(T_E + 460) \ \text{lbm/ft}^3$$

$$\dot{M}_a = 89.60\,(\Delta p_E\, \rho_E)^{0.4842} \ \text{lbm/min}$$

$\dot{M}_e$ = engine exhaust mass flow = $\dot{M}_a + \dot{M}_f/60$ (lbm/min)

E = exhaust flow through tunnel = $E{+}D\left(\frac{E}{E+D}\right) = (E+D)\,\dfrac{(NO_x)_D}{(NO_x)_R}$

FOR HI-VOL SAMPLES ONLY

$\dot{M}_{OR}$ = mass flow of hi-vol sample = $4.65\,(\Delta p_{OR}\, \rho_{OR})^{0.5}$ lbm/min ; $\rho_{OR} \cong 1.326\, p_a/(T_{OR}+460)$

particulate emission rate (g/hr) = $\dfrac{3600\, G_{AR}}{(\text{time})} \dfrac{(\text{TOTAL EXH. MASS})}{\left(\begin{matrix}\text{TOTAL RAW EXH.}\\ \text{MASS FILTERED}\end{matrix}\right)} = \dfrac{3600\, G_{AR}}{(\text{time})} \dfrac{\sum_{i=1}^{N} (\dot{M}_e)_i (\text{time})_i}{\sum_{i=1}^{N} (\dot{M}_{OR})_i (\text{time})_i \left(\frac{E}{E+D}\right)_i}$

particulate concentration (mg/m^3 @ 29.92 in Hg ; 21 °C) = $\dfrac{1.586 \times 10^{8}\, G_{AR}}{\sum_{i=1}^{N} (\dot{M}_{OR})_i (\text{time})_i \left(\frac{E}{E+D}\right)_i}$

FOR 47 mm (TUNNEL) SAMPLES ONLY

integrated mass flow through filter j = m_j (lb$_m$)

m_1(filter 1) = 0.0753 $(V_{21}-V_{11})$ lb$_m$

m_2(filter 2) = 0.0767 $(V_{22}-V_{12})$ lb$_m$

m_3(filter 3) = 0.0759 $(V_{23}-V_{13})$ lb$_m$

m_4(filter 4) = 0.0755 $(V_{24}-V_{14})$ lb$_m$

$$\text{particulate emission rate } (\text{g/hr}) = \frac{60\ G_{47j}}{(\text{time})}\ \frac{\sum_{i=1}^{N}(\dot{M}_e)_i\,(\text{time})_i}{\frac{m_j}{(\text{time})}\sum_{i=1}^{N}(\text{time})_i\left(\frac{E}{E+D}\right)_i}$$

$$= \frac{60\ G_{47j}}{m_j}\ \frac{\sum_{i=1}^{N}(\dot{M}_e)_i\,(\text{time})_i}{\sum_{i=1}^{N}(\text{time})_i\left(\frac{E}{E+D}\right)_i}$$

$$\text{particulate concentration } (\text{mg/m}^3\text{ @ 29.92 in Hg \& 21°C}) = \frac{(2.643\times10^{6})\ G_{47j}\ (\text{time})}{m_j\sum_{i=1}^{N}(\text{time})_i\left(\frac{E}{E+D}\right)_i}$$

FOR ERC 47 mm SAMPLES ONLY (steady - state conditions only)

$$\text{particulate emission rate } (\text{g/hr}) = \frac{(9.68\times10^{7})\ G_{ERC}}{(\text{time})}$$

$$\text{particulate concentration } (\text{mg/m}^3\text{ @ 29.92 in Hg \& 21°C}) = \frac{(4.263\times10^{12})\ G_{ERC}}{\dot{M}_e\ (\text{time})}$$

PAGE 1 OF 2

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

RUN NO.	SEQ	DATE	RPM	LOAD	FILTER CODES BY POSITION NO. 1 – R	NO. 2	NO. 3	NO. 4	NO. 5	ENGINE CODE
d – d d d		mm / d d / y y	d d d d	d d d	a a d d – d d d d					
–	0 1	/ /			–	–	–	–	–	

	PARTICULATE WEIGHTS									
FUEL CODE	GAR OR G471	G472	G473	G474	GERC	PA	CB	TOTAL TIME		N
d d d	d . d d d d d d					d d . d d	d d d d d	d d d d . d		d d
0 2 E M F										

DRY GAS METER READINGS

V11	V21	V12	V22	V13	V23	V14	V24
d d d . d d d							
0 3							

TIME IN MODE

	1	2	3	4	5	6	7	8	9	10	11	12	13
	d d d												
0 4 T I M E													

ORIFICE TEMP. BY MODE

	1	2	3	4	5	6	7	8	9	10	11	12	13
	d d d												
0 5 T O R													

INTAKE AIR TEMP. BY MODE

	1	2	3	4	5	6	7	8	9	10	11	12	13
	d d d												
0 6 T E													

BLOWER INLET TEMP. BY MODE

	1	2	3	4	5	6	7	8	9	10	11	12	13
	d d d												
0 7 T B													

SOUTHWEST RESEARCH INSTITUTE

DEPARTMENT OF EMISSIONS RESEARCH

DIESEL PARTICULATE GRAVIMETRIC ANALYSIS

PROJECT 11-

ENCODED BY

DATE ENCODED

PAGE 2 OF 2

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

ORIFICE ΔP FOR Hi-VOL SAMPLE BY MODE

RUN NO.	SEQ	1	2	3	4	5	6	7	8	9	10	11	12	13
d – d d d		d . d d												
–	0 8 D P O R													

ENGINE FUEL RATE IN LB_m/HR BY MODE

		1	2	3	4	5	6	7	8	9	10	11	12	13
		d d . d												
	0 9 F U E L													

ENGINE AIRFLOW ORIFICE ΔP BY MODE

		1	2	3	4	5	6	7	8	9	10	11	12	13
		d d . d d												
	1 0 D P E													

DILUTE NO_x CONCENTRATION IN PPM BY MODE

		1	2	3	4	5	6	7	8	9	10	11	12	13
		d d d . d												
	1 1 D N O X													

RAW NO_x CONCENTRATION IN PPM BY MODE

		1	2	3	4	5	6	7	8	9	10	11	12	13
		d d d d												
	1 2 R N O X													

```
                PROGRAM RATECC(INPUT,OUTPUT,TAPE60=INPUT)
000003          DIMENSION TOR(13),DPE(13),TE(13),FUEL(13),RNOX(13),DNOX(13)
000003          DIMENSION TB(13),DPOR(13),TIME(13)
000003          DIMENSION EXH(13),AIR(13),FLOWOR(13)
000003          DIMENSION SAMP(4),ENGCODE(2),IFLTRS(5),GJ(5)
000003          EQUIVALENCE (GJ(1),G471),(GJ(2),G472),(GJ(3),G473),(GJ(4),G474)
000003          EQUIVALENCE (GJ(5),GERC)
        C                                           INITIALIZE ARRAYS TO ZERO
000003     301  DO 1 I=1,13
000005            TOR(I)=DPE(I)=TE(I)=FUEL(I)=0
000012            RNOX(I)=DNOX(I)=TB(I)=DPOR(I)=TIME(I)=0
000021            EXH(I)=AIR(I)=FLOWOR(I)=0
000024       1  CONTINUE
        C                                           READ HEADER CARD
000026          READ(60,100)JRUN,JSEQ,JDATE,JRPM,LOAD,IFLTRS,ENGCODE
000047          IF(EOF,60) 80, 2
000052        2 PRINT 200
000056          READ(60,101)KRUN,KSEQ,FUELC,G471,G472,G473,G474,GERC,PA,CB,TOTIME
               1           ,N
000112          PRINT 201,JRUN,JDATE,ENGCODE,FUELC,LOAD,JRPM
        C                                           CHECK FOR FILTERS
000132          IS=1HS
000134          IERC=0
000135          IFCT=1
000136          IF(IFLTRS(2).NE.9H         ) GO TO 3
000140          IS=1H
000141          GO TO 5
000142        3 IFCT=2
000143          IF(IFLTRS(3).NE.9H         )IFCT=3
000146          IF(IFLTRS(4).NE.9H         )IFCT=4
000151          IF(IFLTRS(5).EQ.9H         )GO TO 5
000153          IERC=1
000154          IFCT=5
000155        5 PRINT 202,IS,(L,IFLTRS(L),L=1,IFCT)
        C                                           IF IS=BLANK THEN THIS IS A 8X10
        C                                           SAMPLING SYSTEM.
        C                                           IF IERC=1 THEN THIS IS AN ERC
        C                                           SYSTEM.
        C                                           THERE SHOULD BE A PARTICULATE
        C                                           VALUE FOR EACH FILTER SO LETS
        C                                           GO.
000173          IF(IS.EQ.1H )GAR=G471
000177          PRINT 203,(GJ(L),L=1,IFCT)
000212          IF(IS.EQ.1H ) GO TO 6
000214          PRINT 204
000220        6 IF(KRUN.NE.JRUN.OR.KSEQ.NE.2      )GO TO 8
000230          READ(60,102)KRUN,KSEQ,V11,V21,V12,V22,V13,V23,V14,V24
000257          IF(KRUN.NE.JRUN.OR.KSEQ.NE.3      )GO TO 8
000267          IF(IS.EQ.1H ) GO TO 306
000271          PRINT 205,V11,V21,TOTIME,PA
000304          PRINT 206,V12,V22
000314          PRINT 207,V13,V23
000324          PRINT 208,V14,V24,CB,N
000340          GO TO 7
000341     306  PRINT 218,TOTIME,PA,CB,N
        C                                           READ REST OF DATA FOR ALL MODES
000355        7 READ(60,103)KRUN,KSEQ,(TIME(I),I=1,N)
```

```
000374         IF(KRUN.NE.JRUN.OR.KSEQ.NE.4) GO TO 8
000404         READ(60,104)KRUN,KSEQ,(TOR(I),I=1,N)
000422         IF(KRUN.NE.JRUN.OR.KSEQ.NE.5) GO TO 8
000432         READ(60,105)KRUN,KSEQ,(TE(I),I=1,N)
000450         IF(KRUN.NE.JRUN.OR.KSEQ.NE.6) GO TO 8
000460         READ(60,106)KRUN,KSEQ,(TB(I),I=1,N)
000476         IF(KRUN.NE.JRUN.OR.KSEQ.NE.7) GO TO 8
000506         READ(60,107)KRUN,KSEQ,(DPOR(I),I=1,N)
000524         IF(KRUN.NE.JRUN.OR.KSEQ.NE.8) GO TO 8
000534         READ(60,108)KRUN,KSEQ,(FUEL(I),I=1,N)
000552         IF(KRUN.NE.JRUN.OR.KSEQ.NE.9) GO TO 8
000562         READ(60,109)KRUN,KSEQ,(DPE(I),I=1,N)
000600         IF(KRUN.NE.JRUN.OR.KSEQ.NE.10)GO TO 8
000610         READ(60,110)KRUN,KSEQ,(DNOX(I),I=1,N)
000626         IF(KRUN.NE.JRUN.OR.KSEQ.NE.11)GO TO 8
000636         READ(60,111)KRUN,KSEQ,(RNOX(I),I=1,N)
000654         IF(KRUN.NE.JRUN.OR.KSEQ.NE.12)GO TO 8
         C                                      IF IS=S THEN TOR AND DPOR ARE
         C                                      BLANK
000664         IF(IS.EQ.1HS)  9,10
000670       8 PRINT 209,KRUN,KSEQ
000700         STOP 10
         C                                      4X47 SAMPLE OUTPUT FORMAT
000702       9 PRINT 210
000706         PRINT 211,(TIME(I),DPE(I),TE(I),FUEL(I),RNOX(I),DNOX(I),TB(I)
              1         ,I=1,N)
000735         GO TO 11
000736      10 PRINT 212
000742         PRINT 217,(TIME(I),TOR(I),DPE(I),TE(I),FUEL(I),RNOX(I),DNOX(I)
              1         ,TB(I),DPOR(I),I=1,N)
         C                                      CALCULATIONS COMMON TO ALL
         C                                      SAMPLE TYPES
000775      11 R=CB/TOTIME
000777          DO 12 I=1,N
001001           AIR(I)=102.7*(DPE(I)*PA/(TE(I)+460.))**.4842
001011           EXH(I)=AIR(I)+FUEL(I)/60.
001015      12  CONTINUE
         C                                      CALCULATIONS FOR HI-VOL
001017         IF(IS.EQ.1HS) GO TO 14
001021         SMEXTI=0.
001022         SMFLTN=0.
001023          DO 13 I=1,N
001024           FLOWOR(I)=5.35*(DPOR(I)*PA/(TOR(I)+460.))**.5
001034           SMEXTI=SMEXTI+EXH(I)*TIME(I)
001037           SMFLTN=SMFLTN+FLOWOR(I)*TIME(I)*DNOX(I)/RNOX(I)
001044      13  CONTINUE
001046         PER= 3600.*GAR*SMEXTI/TOTIME/SMFLTN
001053         PRM= PER/GAR
001054         PC= 1.586E+8*GAR/SMFLTN
001056         PCM=PC/GAR
001057         PRINT 213
001062         GO TO 19
         C                                      ERC SYSTEM
001063      14 IF(IERC.NE.1)GO TO 16
001065         PER=9.68E+7*GERC/TOTIME
0 1070         PRM=PER/GERC
001071         SUMEXH=0.
001072          DO 15 I=1,N
```

```
001073             SUMEXH=SUMEXH+EXH(I)
001075        15  CONTINUE
001077           PC=4.263E+12*GERC*N/TOTIME/SUMEXH
001104           PCM=PC/GERC
001105           PRINT 214
001110           GO TO 19
          C                                              4 X 47 SYSTEM
001111        16 V=V21-V11
001113           IF(V.LT.0)V=V+100.
001117           SAMP(1)=.0753*V
001121           V=V22-V12
001123           IF(V.LT.0)V=V+100.
001126           SAMP(2)=.0767*V
001130           V=V23-V13
001132           IF(V.LT.0)V=V+100.
001135           SAMP(3)=.0759*V
001137           V=V24-V14
001141           IF(V.LT.0)V=V+100.
001144           SAMP(4)=.0755*V
001146           SMEXTI=0.
001147           SMTINO=0.
001150            DO 17 I=1,N
001151             SMEXTI=SMEXTI+EXH(I)*TIME(I)
001154             SMTINO=SMTINO+TIME(I)*DNOX(I)/RNOX(I)
001160        17  CONTINUE
001162           RATIO=SMEXTI/SMTINO * 60.
001164           PRINT 215
001170            DO 18 J=1,4
001172             PER= GJ(J)*RATIO/SAMP(J)
001175             PRM= PER/GJ(J)
001177             PC= 2.643E+6*GJ(J)*TOTIME/SMTINO/SAMP(J)
001203             PCM=PC/GJ(J)
001205             PRINT 216,PER,PRM,PC,PCM
001221        18  CONTINUE
001223           GO TO 20
001224        19 PRINT 216,PER,PRM,PC,PCM
001240           IF(G472.NE. 0) GO TO 16
001241        20 GO TO 301
001242        80 STOP 100
          C                                              INPUT FORMATS
001244       100 FORMAT(A5,I2,A8,A4,A3,5A9,A10,A3)
001244       101 FORMAT(A5,I2,A6,5F8.6,F5.2,F6.0,F6.1,8X,I2)
001244       102 FORMAT(A5,I2,8F7.3)
001244       103 FORMAT(A5,I2,5X,13F4.0)
001244       104 FORMAT(A5,I2,5X,13F4.0)
001244       105 FORMAT(A5,I2,5X,13F4.0)
001244       106 FORMAT(A5,I2,5X,13F4.0)
001244       107 FORMAT(A5,I2,5X,13F4.2)
001244       108 FORMAT(A5,I2,5X,13F4.1)
001244       109 FORMAT(A5,I2,4X,13F5.2)
001244       110 FORMAT(A5,I2,4X,13F5.1)
001244       111 FORMAT(A5,I2,4X,13F5.0)
          C                                              OUTPUT FORMATS
001244       200 FORMAT(*1         TABLE          PARTICULATE EMISSION RATE AND CONCEN
               1TRATION CALCULATIONS* )
001244       201 FORMAT(30X,*RUN *,A5,2X,A8 /15X,*ENGINE *,A10,A3,*  FUEL *,A6,
               1         *  LOAD *,A3,*  RPM *,A4 )
001244       202 FORMAT(*0       FILTER*,A1,I2,1X,A9,4(I3,1X,A9))
```

```
001244      203 FORMAT(*0       PARTICLES*,F10.6,4F13.6)
001244      204 FORMAT(*0       DRY GAS METER READINGS  INITIAL   FINAL     TOTAL T
               1IME   ATM PRESSURE*)
001244      205 FORMAT(*                                   1*,F8.3,F9.3,F14.1,F13.2)
001244      206 FORMAT(*                                   2*,F8.3,F9.3)
001244      207 FORMAT(*                                   3*,F8.3,F9.3,    *   BLOWER
               1COUNT  NO. OF MODES*)
001244      208 FORMAT(*                                   4*,F8.3,F9.3,F15.0,I10)
001244      209 FORMAT(* CARD OUT OF SEQUENCE *,A5,I3)
001244      210 FORMAT(*0                TIME    DPE    TE   FUEL     RNOX     DNOX
               1 TB*)
001244      211 FORMAT(*                 *,F4.0,F8.2, F6.0, F7.1,  F9.1,    F9.1,
               1F6.0 )
001244      212 FORMAT(*0       TIME    TOR    DPE    TE   FUEL     RNOX     DNOX
               1 TB   DPOR*)
001244      217 FORMAT(*       *,F4.0,F7.0,F7.2,F6.0, F7.1, F9.1,F9.1,F6.0,F7.2)
001244      213 FORMAT(*0       HI-VOL*)
001244      214 FORMAT(*0       E R C   SYSTEM*)
001244      215 FORMAT(*0       4 X 47  SYSTEM*)
001244      216 FORMAT(*0                PARTICULATE EMISSION RATE =* ,F12.2/
               1        *                            MULTIPLIER    =* ,F10.0/
               2        *                PARTICULATE CONCENTRATION =* ,F10.0/
               3        *                            MULTIPLIER    =* ,F10.0 )
001244      218 FORMAT(*0       TOTAL TIME   ATM PRESSURE   BLOWER COUNT   NO. OF M
               1ODES*/          F17.1      ,F15.2          ,F15.0          ,I12)
001244          END
```

```
TABLE         PARTICULATE EMISSION RATE AND CONCENTRATION CALCULATIONS
                         RUN 2-000  08/21/74
        ENGINE D.D.6L71-T       FUEL EM198F  LOAD       RPM COMP

FILTERS 1 FP47-168    2  A47-179    3  A47-180    4  A47-181

PARTICLES    .000929        .001838        .001873        .001911

DRY GAS METER READINGS  INITIAL     FINAL      TOTAL TIME   ATH PRESSURE
                      1    8.630    16.157        2374.3        29.48
                      2   43.643    62.840
                      3   71,358    90.827     BLOWER COUNT  NO. OF MODES
                      4   58,338    78.432          64801         11

       TIME      DPE      TE    FUEL       RNOX       DNOX     TB
       198      2.00      67    11.0      785.0        3.9     75
       183      2.30      67    23.0      240.0       11.2     75
       208      2.70      69    45.0      503.0       24.7     80
       222      3.40      68    68.0      855.0       44.6     86
       240      4.30      69    85.0     1152.0       63.5     95
       182       .15      70     1.5      191.0        5.9     90
       235      8.40      71   104.0     1172.0       93.5     94
       238      6.80      71    78.0      883.0       63.5    109
       234      5.50      72    59.0      541.0       34.8    106
       216      4.50      70    44.0      273.0       16.3     99
       219      3.80      70    19.0      965.0        6.1     93

4 X 47  SYSTEM

         PARTICULATE EMISSION RATE =         99.18
                     MULTIPLIER    =     106762
         PARTICULATE CONCENTRATION =      89157
                     MULTIPLIER    =   95970825

         PARTICULATE EMISSION RATE =         75.54
                     MULTIPLIER    =      41096
         PARTICULATE CONCENTRATION =      67900
                     MULTIPLIER    =   36942594

         PARTICULATE EMISSION RATE =         76.70
                     MULTIPLIER    =      40949
         PARTICULATE CONCENTRATION =      68946
                     MULTIPLIER    =   36810414

         PARTICULATE EMISSION RATE =         76.22
                     MULTIPLIER    =      39886
         PARTICULATE CONCENTRATION =      68518
                     MULTIPLIER    =   35854426
```

```
TABLE         PARTICULATE EMISSION RATE AND CONCENTRATION CALCULATIONS
                              RUN 3-000  08/13/74
        ENGINE D.D.6L71-T       FUEL EM198F  LOAD        RPM COMP

FILTER  1   AR-73

PARTICLES    .09790U

TOTAL TIME    ATM PRESSURE   BLOWER COUNT   NO. OF MODES
   2375.5           29.95          64968         11

TIME    TOR     DPE    TE   FUEL     RNOX      DNOX   TB    DPOR
198      76    1.85    72    4.0     80.0       3.5   79    2.05
183      84    2.00    72   22.0    235.0      10.3   81    2.05
208      88    2.30    72   40.0    495.0      22.5   85    2.05
222      92    3.20    73   65.0    830.0      42.0   90    2.05
240      96    3.90    76   81.0   1050.0      58.0   99    2.05
182      99     .14    76    2.0    220.0       6.2   92    2.05
235     101    7.50    76  102.0   1037.0      80.0  105    2.05
238     106    6.50    77   80.0    825.0      59.0  110    2.05
234     108    5.20    78   61.0    520.0      31.0  107    2.05
216     107    4.30    79   28.0    262.0      14.5  101    2.05
219     105    3.60    77   20.0    100.0       5.2   95    2.05

HI-VOL

        PARTICULATE EMISSION RATE =        73.14
                    MULTIPLIER    =        747
        PARTICULATE CONCENTRATION =      60832
                    MULTIPLIER    =     703084
```

Appendix B3/11

SOUTHWEST RESEARCH INSTITUTE
8500 CULEBRA ROAD • POST OFFICE DRAWER 28510 • SAN ANTONIO, TEXAS 78284

September 10, 1974

TO: Dr. Ronald Bradow, Project Officer
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

FROM: Charles T. Hare and Karl J. Springer
Department of Emissions Research
Southwest Research Institute
8500 Culebra Road
San Antonio, Texas 78284

SUBJECT: Monthly Progress Report No. 14 for the period August 1 to August 31, 1974; Contract No. 68-02-1230, "Development of a Methodology for Determination of the Effects of Diesel Fuel and Fuel Additives on Particulate Emissions," SwRI Project No. 11-3718.

PREPARED FOR: Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Introduction

The purpose of this project is to develop and demonstrate a test procedure suitable for characterizing the effects of diesel fuels and fuel additives on particulate emissions from automotive (truck and bus) diesels. The scope of this work includes construction and use of a dilution tunnel for diesel exhaust, use of a variety of particulate sampling devices and techniques, and application of a wide range of chemical analyses to diesel particulate. This report covers the test protocol which has been developed to meet project objectives, including all assumptions and calculation techniques.

Progress During the Period August 1 to August 31, 1974

The initial batches of samples have been analyzed gravimetrically, and a number of samples have also been analyzed for total organic solubles, BaP, IR spectrum, S-C-H-N, and metals. Several samples of organic solubles have also been analyzed for S-C-H-N-O and hydrocarbon boiling point distribution. This progress report contains these initial analytical results; and while some "gaps" certainly exist at this point, the data show some very interesting trends.

Initial Gravimetric Results, Detroit Diesel 6L-71T

A gravimetric determination is being made on every filter run during this program, with resolution to 1 μg of particulate for 47mm filters and to 0.1mg for rectangular (hi-vol) filters. A computer program has been set up to calculate total engine emissions in g/hr and raw exhaust particulate concentrations in $\mu g/m^3$ from the particulate weights and operating variables. A number of samples have been processed by computer, mostly those collected on hi-vol filters, and average results available at this point are summarized in Table 1. Note that concentrations are expressed in mg/m^3 rather than $\mu g/m^3$ to make the numbers easier to handle. For the few runs already processed using 47mm filters, agreement with the hi-vol results seems reasonably good.

Initial S, C, H, N, and O Results, Detroit Diesel 6L-71T

Quantitative determinations of S, C, H, and N on 20 sets of filters were conducted by Galbraith Laboratories, along with quantitative S, C, H, N and O on 4 samples of organic solubles. The results exhibited quite a bit of variability, some of which was expected due to the range of operating conditions and fuels used. The values submitted by Galbraith are presented in Tables 2 and 3. Although no detailed analysis has been conducted, it appears that the particulate samples from runs on fuel B exhibit higher sulfur content than those from runs on fuel C. It also appears that the particulate carbon content is higher for fuel C than for fuel B.

Initial Results on Total Organic Solubles and BaP

As at the end of the reporting period, total organic solubles and BaP have been determined for 10 samples. Results of repeatability checks and "spiked" filter runs are not available now, but they should be by the end of September. Organic solubles / BaP results are given in Table 4, in addition to emission rates and raw exhaust concentrations of BaP calculated from (tentative) operating data. Variability in the BaP data is rather high, and it is hoped that some of the "checks" noted above will point out some of the sources of variation.

Initial Results of Analysis for Particulate Metal Content

Rather than re-tabulate the data on metals found in 14 samples by Scanning Electron Analysis Laboratories, their data as submitted have been reproduced and are included as Appendix page A-2. Thus far, no functional relationship between metal content and operating condition has been discovered, but more data should help to illuminate this area. With the exceptions of lead in two samples and an (apparently fluke) amount of Barium in one sample, Zinc is the only element found in substantial quantity. It is suspected that this material may originate in the lubricating oil, and procedures are being instituted to check on this suspicion. The

TABLE 1. INITIAL AVERAGE* GRAVIMETRIC RESULTS, HI-VOL (GLASS FIBER) FILTERS USED FOR TESTS ON DETROIT DIESEL 6L-71T

	Fuel B		Fuel C		Fuel A		Fuel A + DII-2	
Operating Condition	g/hr	mg/m^3	g/hr	mg/m^3	g/hr	mg/m^3	g/hr	mg/m^3
Idle	9.16	45.6	7.8**	36.**	3.9	21.	4.3	20.
1600 rpm - 0% load	42.2	55.0	41.6	54.3	---	---	---	--
1600 rpm - 25% load	48.	62.	62.	74.	---	---	---	--
1600 rpm - 50% load	83.**	95.**	76.2	84.4	59.	65.	62.	67.
1600 rpm - 75% load	87.	88.	78.	77.	---	---	---	---
1600 rpm - 100% load	102.	89.0	89.	77.	---	---	---	--
2100 rpm - 0% load	63.4	59.6	72.	67.	---	---	---	--
2100 rpm - 25% load	69.	61.	34.	29.	---	---	---	--
2100 rpm - 50% load	114.	89.8	110.	89.	---	---	---	--
2100 rpm - 75% load	110.	80.	120.	85.	---	---	---	--
2100 rpm - 100% load	144.	90.4	---	--	---	---	---	--
Composite	86.7	79.0	76.4	71.9	82.	76.	76.1	69.4

*points representing only one run contain 2 significant figures

**unacceptable variability, 2 significant figures shown

TABLE 2. INITIAL SINGLE VALUES FOR S, C, H, N, AND O IN ORGANIC SOLUBLES SAMPLES BY OPERATING CONDITION, DETROIT DIESEL 6L-71T ENGINE AND FUEL B

Operating Condition	Percent of Species by Weight in Organic Solubles					Σ%
	C	H	N	S	O	
Idle	85.5	13.2	0.20	0.32	0.73	100.0
1600 rpm - 50% load	83.3	12.8	0.36	0.18	3.4	100.0
2100 rpm - 100% load	78.8	11.7	0.70	0.25	8.4	99.8
Composite	82.0	12.4	0.20	0.77	4.5	99.9

TABLE 3. INITIAL SINGLE VALUES FOR S, C, H, AND N IN PARTICULATE SAMPLES BY OPERATING CONDITION, DETROIT DIESEL 6L-71T ENGINE

Operating Condition	Wt. % - Fuel B				Σ%	Wt. % - Fuel C				Σ%
	C	H	N	S		C	H	N	S	
Idle	60.9	7.7	<0.1	3.0	71.6	68.4	9.1	<0.1	2.1	79.6
1600 rpm - 0% load	69.1	10.3	1.0	2.1	82.5	73.3	11.1	0.1	0.7	85.2
1600 rpm - 25% load	76.8	12.8	1.0	2.6	93.2	--	--	--	--	--
1600 rpm - 50% load	63.5	10.9	<0.1	2.9	77.3	77.2	10.7	0.3	0.6	88.8
1600 rpm - 75% load	71.1	10.5	0.3	2.1	84.0	--	--	--	--	--
1600 rpm - 100% load	66.7	8.8	0.8	2.3	78.6	75.0	? *	0.1	0.5	? *
2100 rpm - 0% load	66.6	9.8	0.8	1.8	79.0	72.7	9.7	0.9	1.0	84.3
2100 rpm - 25% load	65.9	10.4	<0.1	2.8	79.1	--	--	--	--	--
2100 rpm - 50% load	65.8	9.8	<0.1	2.4	78.0	77.6	11.7	0.6	0.6	90.5
2100 rpm - 75% load	69.9	? *	<0.1	1.6	? *	--	--	--	--	--
2100 rpm - 100% load	70.7	10.9	0.4	2.2	84.0	74.5	12.0	<0.1	0.9	87.4
Composite	71.8	10.0	0.3	2.0	84.1	75.0	11.3	<0.1	1.7	88.0

*indicates questionable data

TABLE 4. INITIAL DETERMINATIONS OF TOTAL ORGANIC SOLUBLES AND BaP, DETROIT DIESEL 6L-71T ENGINE

	wt. % BaP in Extract			wt. % BaP in Particulate		
Operating Condition	**Fuel A**	**Fuel B**	**Fuel C**	**Fuel A**	**Fuel B**	**Fuel C**
Idle	0.0247	0.0126	0.0148	0.0093	0.0036	0.0063
1600 rpm - 50% load	0.0188	0.0122	0.0172	0.0136	0.0061	0.0124
2100 rpm - 100% load	---	0.0127	---	---	0.0066	---
Composite	0.0137	0.0265	0.0088	0.0087	0.0117	0.0054

	BaP Emissions, µg/hr			BaP Conc., µg/m^3		
Operating Condition	**Fuel A**	**Fuel B**	**Fuel C**	**Fuel A**	**Fuel B**	**Fuel C**
Idle	365.	299.	256.	2.00	1.58	1.44
1600 rpm - 50% load	7980.	4160.	9120.	8.82	4.79	10.2
2100 rpm - 100% load	---	9880.	---	---	6.20	---
Composite	7170.	9600.	3950.	6.64	9.01	3.72

data on metals are expected to be more revealing when fuels with metal-containing additives are used.

IR Spectra and Paraffin Boiling Point Distribution

Infrared spectra have been run on the same samples for which BaP data were presented, but the traces have not yet been reduced in size sufficiently for inclusion in this report. The major results appearing so far seem to be indications of some carbonyl and hydroxyl groups, but solvent interference is causing problems in some areas of the trace. Efforts are being made to refine the technique where necessary.

Separation of the paraffin fraction from the remainder of the organic solubles is going well, and a few samples have been analyzed chromatographically. It appears thus far that most of the paraffins are out of the normal diesel fuel range (nominal C_{26} as compared to nominal C_{16} for fuel), and work is underway to come up with a tracer compound which should tell us whether or not the paraffins are related to the lubricating oil. The major problem with the tracer thus far is that components like n-tetracontane (C_{40}) would cost some $1000 for enough to treat the oil at a 1% level.

Project Schedule

Despite good faith efforts to conclude the technical effort within the time allotted under modification no. 1 to the contract (68-02-1230), it now appears that another no-additional-cost time extension will be necessary to accommodate the test operations. The current date for the end of the technical effort is October 23, 1974, and the date for end of contract is February 22, 1975. The memorandum initiating action to request a three-month extension on the above basis has been submitted, and a copy is included as page A-3 of the Appendix.

Possible Problems and Corrective Action

The only problem remaining at this time is interferences in the Phenol analysis, and action is being taken to find a solution. Several filter treatments and new environmental control for the filters are being tried, and the results should be available during the next reporting period.

Plans for the Next Reporting Period

It is planned that sample acquisition and analysis will be continued, and that all gaseous emissions and smoke tests on the Detroit Diesel 6L-71T engine be completed.

Submitted by:

Charles T. Hare

Charles T. Hare
Manager, Advanced Technology
Department of Emissions Research

Karl J Springer

Karl J. Springer
Manager
Department of Emissions Research

RESULTS OF X-RAY FLUORESCENT ANALYSIS
DIESEL EXHAUST PARTICULATE ON FLUOROPORE FILTERS
(in micrograms per square centimeter)*

ELEMENT	Ca	V	Mn	Ni	Cu	Zn	Pb	Sr	Sn	Ba
M.D.L.**	1.70	0.36	0.49	0.16	0.10	0.12	0.22	0.22	0.62	2.59
Sample Identification										
S-1 FP47-107	-	-	-	-	-	3.00	-	-	-	-
S-2 FP47-113	-	-	-	-	-	1.94	-	-	-	-
S-3 FP47-105	-	-	-	-	-	0.54	tr	-	-	-
S-4 FP47-141	-	-	tr	-	-	0.57	tr	-	-	-
S-5 FP47-142	-	-	-	-	-	2.49	0.39	-	-	2.80
S-6 FP47-144	-	-	-	-	-	3.16	-	-	tr	tr
S-7 FP47-145***	-	-	-	-	-	0.87	0.30	-	-	-
S-8 FP47-170	-	-	-	-	-	1.29	tr	-	-	tr
S-9 FP47-171	-	-	tr	-	-	0.33	-	-	-	-
S-10 FP47-172	-	-	-	-	-	2.85	tr	-	-	-
S-11 FP47-174	-	-	tr	-	-	6.09	tr	-	-	tr
S-12 FP47-175	-	-	-	-	-	1.89	tr	-	-	-
S-13 FP47-166	-	-	-	-	-	2.95	tr	-	-	-
S-14 FP47-168	-	-	tr	tr	-	1.95	tr	-	-	-

* Analyses in which counts were obtained for an element but were equivalent to less than the minimum detectable limit are noted by "tr" (trace); a "-" denotes that no X-ray counts were detected.

** Minimum detectable limit $= \left[\frac{2\sqrt{\text{Background Counts}}}{\text{Peak Counts}} \right] \times (\text{Concentration})$

*** Estimated 1.0 $\mu g/cm^2$ iron present

MEMORANDUM September 20, 1974

FROM: Charles T. Hare

TO: Vince Krause

RE: Project 11-3718, Contract 68-02-1230
Request for time extension at no additional cost

We would like to request a 3-month time extension at no additional cost to the sponsor on Contract No. 68-02-1230. The reasons for this request are:

1. technical difficulty with development of and contracting for chemical analytical procedures;
2. longer-than-anticipated tests to acquire adequate sample for analysis; and
3. late delivery of Government-furnished property (ERC sampler)

The requested extension would move the end of the technical effort to about January 22, 1975, and the end of the contract to about May 22, 1975. It is anticipated that this schedule can be met if no further problems develop.

cc: Ron Bradow

Appendix B3.12

SOUTHWEST RESEARCH INSTITUTE
8500 CULEBRA ROAD • POST OFFICE DRAWER 28510 • SAN ANTONIO, TEXAS 78284

September 9, 1974

TO: Dr. Ron Bradow, Project Officer
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

FROM: Charles M. Urban, Harry E. Dietzmann
and Karl J. Springer
Department of Emissions Research
Southwest Research Institute
San Antonio, Texas 78284

SUBJECT: Monthly Progress Report No. 7 for the period August 1, 1974 through August 31, 1974; Contract No. 68-02-1275, "Protocol to Characterize Gaseous Emissions as a Function of Fuel and Additive Composition;" SwRI Project No. 11-3902-001.

PREPARED FOR: Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Introduction

The purpose of this project is to develop test methods and overall test protocols to characterize potentially harmful gaseous emissions from automobiles as a function of fuel and fuel additive composition. The scope of this work includes the selection and application of analytical techniques to automobile exhaust to determine various gaseous sulfur, nitrogen and hydrocarbon compounds. These methods will then be applied to the exhaust from two 350 CID Chevrolet engines, one standard and one with a prototype catalytic converter, at the accomplishment of 1000 and 2000 mile intervals of operation under the LA-4 cycle conditions.

Progress During the Period August 1 through August 31, 1974

Phase I - Chemical Analytical Procedure Development and Demonstration

Sulfur Dioxide (SO_2) - During the past reporting period, a number of experiments were conducted to determine the extent of individual exhaust gas component interferences. The results of these experiments are presented as Appendix A to this report. Two SO_2 span gases (balance Air) are in hand and once the manufacturer certified analysis is verified, a sulfur balance will be conducted. Current plans call for continuous SO_2 sampling during the 1975 LD FTP, with an on line integrator to determine average SO_2 concentrations in each of the three portions of the LA-4 test. Sulfur dioxide emission rates will be calculated in grams/kilometer just as NO_x, HC and CO.

It is planned to use air balance span gases and air zero gas as the routine calibration gases for this instrument, since exhaust samples will be air rich and relatively high in oxygen content. As documented in Appendix A, using the Model 40 pulsed fluorescent analyzer in systems with high oxygen concentrations (15-20 percent) minimizes any interferences that may otherwise create problems. The Model 40 SO_2 instrument thus far has performed satisfactory and the instrument may be considered available for routine testing.

Sulfur Trioxide (SO_3) - A satisfactory barium chloranilate column has been prepared and the high pressure liquid chromatograph (HPLC) system is deemed ready for routine testing. Exhaust samples have been obtained and analyzed using the procedure developed by EPA Research Triangle Park. A Beckman model 25 UV-VIS recording spectrophotometer, equipped with a flow-through cell, is being used as the detector. Several samples will be obtained during the qualification runs and sulfur balance tests. Calculations for $SO_4^=$ emission rates will be made and reported in g/km.

Although this procedure has been readily adopted for un-leaded fuel, it is expected that an additional ion-exchange column will be necessary to remove any anions in the extracted sample. Several references to the original procedure developed at EPA have shown that anions such as F^-, Cl^-, Br^- interfere with the barium chloranilate - $SO_4^=$ reaction.

Non-Reactive Hydrocarbons (NRHC) - The NRHC system is ready for routine testing and will be used during the qualification runs.

Polynuclear Organic Matter (POM) - During the last reporting period, two fluoropore filters were loaded during four LA-4 runs. The filters were extracted using a soxhlet extraction and reduced to a constant volume and analyzed using the CAPE-7-68 DOAS instrument for aromatic content. Using isokinetic sampling flow rates, a total of 125 ft^3 was sampled with the two filters. Assuming about a 6:1 dilution ratio, only 21 ft^3 of raw exhaust was actually obtained. In reviewing work performed using the CAPE-6-68 polynuclear aromatic analysis of exhaust, it was apparent that a tremendous quantity of exhaust was required for sample collection. Two references (1,2)* which used the analytical methods developed under the CAPE-6-68 program, used the entire exhaust rather than a small isokinetic sample. Those samples were collected using 3 blocks of 12 seven-mode tests, giving a total of 36 seven-mode tests per sample collected. Also, these samples were collected using the entire exhaust stream except for a small stream diverted for instrumental analysis. Using this sampling procedure and testing sequence, it is estimated that well over 4000 ft^3 of raw exhaust was collected. In reviewing the overall project requirements, it is estimated that by modification to the existing sampling interface to include four filter systems and increasing the sample volumes ten-fold, a total of over 40 LA-4 runs would be required for each test condition.

---

*Superscript numbers refer to list of References at the end of this report

With the concurrence of the project officer, plans have been made to delete the analysis of polynuclear organic matter (POM) from the project performance plan. Retaining the analysis of POM in the performance would severely delay the program schedule.

H_2S, COS, and Lower Mercaptans - A short column of Chromosorb 102 appears to be quite satisfactory for SO_2 and COS using the Flame Photometric Detector. Although dilute concentrations of COS are readily made, considerable difficulty has been encountered with the more polar and reactive H_2S. An all teflon system using Teflon sample bags is best. Figure 1 shows a chromatogram of a 10 ml sample containing 100 ppb each of H_2S and COS.

Nitrogen Compounds - Efforts to obtain a column to do ammonia, nitromethane, and dimethylnitrosamine have been unsuccessful. The Chromosorb 104 which looked hopeful for this purpose had an extremely high bleed level and was impossible to use. Contact was made with the manufacturer. They suggested some solvent washings which were tried, but produced little improvement. The manufacturer is going to send a new Chromosorb 104 from a different batch. It appears, however, that chromatographic conditions for ammonia and nitromethane are not compatible. It appears the best approach is to use the Chromosorb 101 for nitromethane and dimethylnitrosamine. Figure 2 shows a chromatogram of 1 ng each of nitromethane and dimethylnitrosamine using the Hall Electrolytic Conductivity Detector and Chromosorb 101 programmed from 100°C to 170°C at 10° per minute.

Phase II - Setup, Conditioning, and Qualification of Fuel/Additive Test Engines

During the past reporting, qualification testing has been completed on test stand 2, the 1972 350 V-8 Chevrolet engine. A total of two cold starts and four force cooled starts have been run and the results along with the original contract specifications are presented in Table 1 and are summarized as follows:

1975 LD FTP Emission Rates	EPA Specifications Max	Min	SwRI Emission Results Cold Start	Force Cooled
HC, g/km	2.5	1.5	2.1	1.9
CO, g/km	22	12	26.3	22.2
NO_x, g/km	2.5	1.9	1.7	1.7

These tests were conducted with the program test fuel doped with thiophene to obtain the target sulfur level of 0.1 percent. As observed, the range of HC (g/km) specified by EPA was 2.5-1.5 g/km and the cold start and force cooled tests were both within the EPA emissions specifications. EPA specified CO emission rates ranged between 22 and 12 g/km. The CO and HC emissions were only slightly higher in the cold starts than in the force cooled starts. Due to the nature of this project and the method of mileage accumulation, it is recommeded that either force cooled or hot starts be used during Phase III emission testing. Although there was no difference in the NO_x emission rates using both cold starts and force cooled tests, NO_x was slightly less than the minimum contract specifications.

The force cooled starts were conducted using a given set of predetermined conditions to insure repeatable test conditions. After the initial cold start had been completed, the engine was shut off and cooling water was forced through the engine. A fan was used to force lab air over the engine and once the engine had been cooled down and remained stable at not more than 3°F above ambient temperature, the engine was ready for 1975 LD FTP testing. Similar force cooling procedures have been used quite satisfactory in other projects.

An alternative procedure for conducting the Phase III emission testing would be using a hot start rather than force cooled or cold starts. A procedure could be readily devised for obtaining repeatable hot start emission data should this approach be selected. One advantage of using hot starts would be to enable the tunnel to be pre-heated to a consistent temperature. This could aid in the preservation of sample integrity, especially for the reactive sulfur containing compounds during the start-up and initial warm-up period of the tunnel prior to the CVS. It is uncertain as to the fate of SO_2 and SO_3 if the tunnel wall temperature changes significantly during the first 505 seconds of the 1975 LD FTP. This uncertainty could be eliminated if hot starts are used exclusively during the Phase III testing.

During the last reporting period, the GM-catalyst has been received and installed on the prototype 1975 350 V-8 Chevrolet engine on stand 1. At the present time, the catalysts are undergoing preliminary break-in prior to qualification emission testing. It is expected that qualification testing will be completed during the second week in September. Once the qualification testing is complete, a sulfur balance will be conducted on both engines using the 1975 LD FTP. During the sulfur balance tests sulfur dioxide and sulfur trioxide (sulfate) emission levels will be obtained. It is not expected that H_2S, COS or mercaptans will significantly affect the sulfur balance. Once the qualification testing and the sulfur balance has been completed, both engines will be ready for mileage accumulation.

Current Problems

Insufficient sample acquisition of polynuclear organic matter on a filter media during a reasonable number of LA-4 tests has deleted this analysis from the testing schedule. Analysis of H_2S, COS and nitrogen compounds is progressing slowly and hopefully will be ready for routine analysis once the qualification runs have been completed.

Work to be Performed During the Next Reporting Period

Qualification testing on both engines is expected to be complete during the next reporting period. A sulfur balance will be obtained on both engines during LA-4 testing to validate both the SO_2 and SO_3 sampling systems. It is expected that full scale demonstration of all sampling and analytical methods will be accomplished, as well as initiation of mileage accumulation on the first additive package.

Prepared by:

Charles Urban

Charles M. Urban
Senior Research Engineer
Department of Emissions Research

and

Harry E. Dietzmann

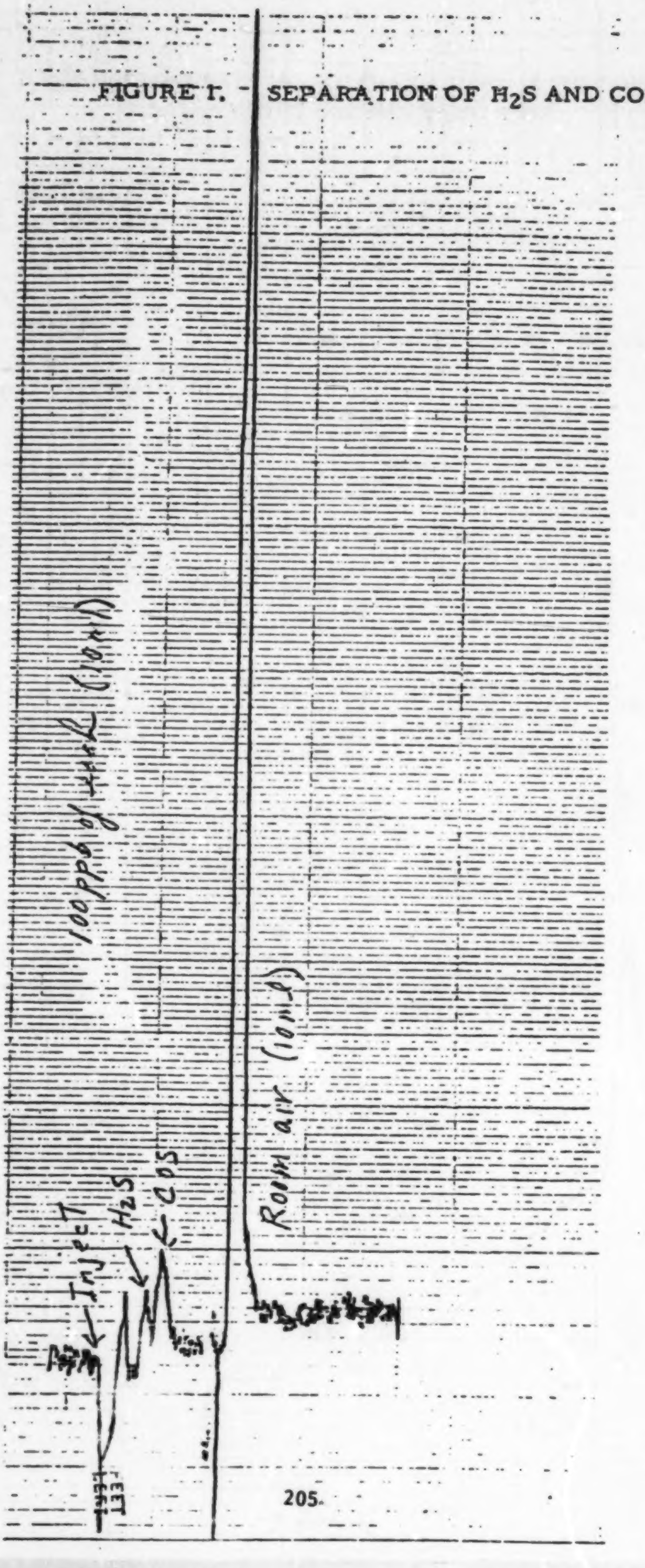
Harry E. Dietzmann
Senior Research Chemist
Department of Emissions Research

Submitted by:

Karl J. Springer

Karl J. Springer
Director
Department of Emissions Research

FIGURE 1. SEPARATION OF H_2S AND COS



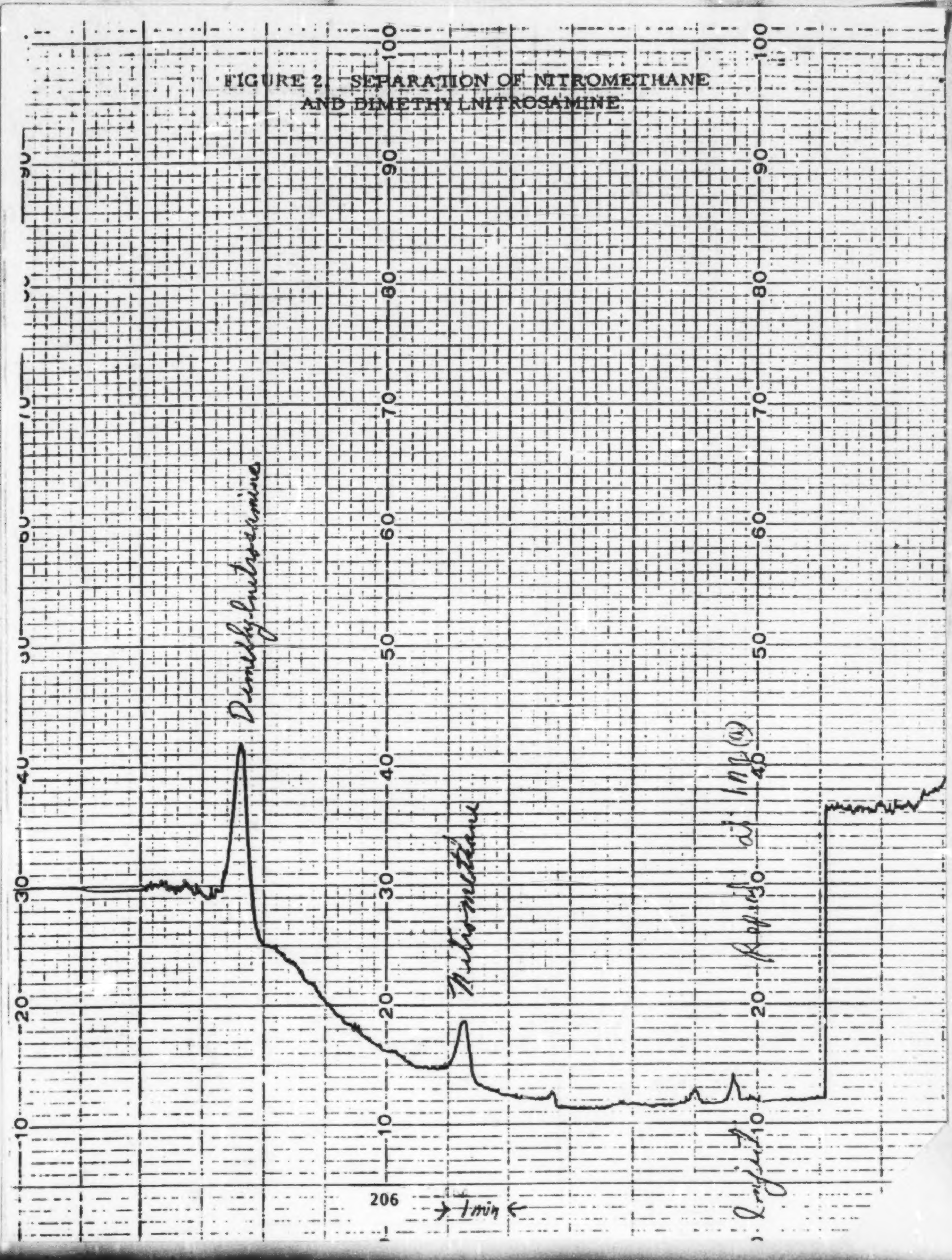


FIGURE 2. SEPARATION OF NITROMETHANE AND DIMETHYLNITROSAMINE

TABLE 1. PRELIMINARY QUALIFICATION EMISSION RESULTS (1972 350 CID CHEVROLET ENGINE - STAND 2)

Type of Start	Date	Run	1975 LD FTP Emission Rate, g/km HC	CO	NO_x
Cold Start	8-27-74	1	2.06	26.16	1.74
Cold Start	8-28-74	1	2.05	26.43	1.60
Force Cooled	8-27-74	2	1.82	21.99	1.58
Force Cooled	8-27-74	3	1.79	23.54	1.71
Force Cooled	8-27-74	4	2.00	21.84	1.84
Force Cooled	8-28-74	2	2.05	21.27	1.62

LIST OF REFERENCES

1. Gross, George P., "The Effect of Fuel and Vehicle Variables on Polynuclear Aromatic Hydrocarbon and Phenol Emissions," SAE paper 720210, presented at the SAE Automotive Engineering Congress - Detroit, Michigan - January 10-14, 1972.

2. Hoffman, C. S., et al, "Polynuclear Aromatic Hydrocarbon Emissions from Vehicles," presented before the Division of Petroleum Chemistry, Inc., American Chemical Society, Los Angeles Meeting, March 28-April 2, 1971.

APPENDIX A

MODEL 40 PULSED FLUORESCENT SO_2 ANALYZER INTERFERENCES

MODEL 40 PULSED FLUORESCENT SO_2 ANALYZER INTERFERENCES

The use of the model 40 pulsed fluorescent SO_2 analyzer in the presence of other exhaust gas components could cause potential interference problems. The intended use of this instrument will be in sampling CVS exhaust on a continuous basis. Since the exhaust will be essentially an air-based sample, the experiments described are orientated toward this particular application.

CO and CO_2 Interferences

Initial CO and CO_2 interference checks were conducted using a single bottle cart containing eight golden standards named by EPA Ann Arbor. This group of bottles contained multi-component blends as well as single component mixtures. All eight bottles contained nitrogen as a balance gas. The first set of data was obtained using standard regulators with neophrene diaphragms and teflon tubing. The results of these tests are found in Table A-1. Response as SO_2 ranged from 10.3 to 17.5 ppm with no apparent correlation for response as ppm SO_2 and interference concentration. The CO concentrations varied from 0.48 to 9.58 percent, while the CO_2 values ranged from 5.7 to 15.23 percent.

TABLE A-1. MULTICOMPONENT BLENDS OF CO AND CO_2/N_2 RESPONSE AS SO_2 IN MODEL 40 PULSED FLUORESCENT ANALYZER (NORMAL NEOPHRENE DIAPHRAGM REGULATOR)

Test	Concentration, %* CO	CO_2	Response as ppm SO_2
1	9.58	5.70	15.5
2	-	14.16	10.3
3	-	12.36	16.0
4	-	11.22	16.5
5	5.39	10.46	17.5
6	2.79	13.18	17.0
7	1.39	-	16.5
8	0.48	15.23	17.5

*balance gas N_2

Since it was obvious that something other than a straightforward single compound interference was involved, additional experiments to determine the extent of other variables that might lead to apparent interferences were conducted. The first such variable checked was the effect of regulator diaphragm type on the response as ppm SO_2. Since other data was previously run and substantial data available for neophrene regulator diaphragms, it was decided to investigate the response of several of the previously tested bottles using metal diaphragm regulators like those used for hydrocarbon span gases. The results of this experiment are found in Table A-2. Although it is difficult to make any definite conclusions, it was observed that the response as ppm SO_2 for these same three CO/CO_2 bottles was 2.5 to 3.0 ppm less for the metal diaphragm.

TABLE A-2. MULTICOMPONENT BLENDS OF CO AND CO_2/N_2 RESPONSE AS SO_2 IN MODEL 40 PULSED FLUORESCENT ANALYZER (METAL DIAPHRAGM REGULATOR)

Test	Concentration, %* CO	Concentration, %* CO_2	Response as ppm SO_2
1	9.58	5.70	13.0
2	5.39	10.46	14.5
3	0.48	15.23	15.0

*balance gas N_2

The next item checked was CO_2 in balance zero air. A clean Tedlar bag was prepared with a double end shut off quick connect and filled with zero air. The bag sample was then analyzed in the Model 40 SO_2 instrument and no response was observed. The bag was then doped with some pure CO_2 to give a CO_2 concentration of about 13 percent. The bag was then run in the SO_2 instrument and still no response was observed. As a result of this experiment, it was obvious that CO_2 alone could not be considered to be an interference compound; however, in conjunction with other species could present interference problems. At this point, two facts were apparent; first, CO_2/N blends gave 10-16 ppm SO_2 response and secondly, CO_2/Air blends gave no response.

To determine the extent of the CO_2/N_2 interference, additional experiments were conducted. The availability of a range of O_2/N_2 blends was used to narrow down this problem. The bottles were N_2 zero gas, 5 percent O_2/95 percent N_2, 10 percent O_2/90 percent N_2, 15 percent O_2/85 percent N_2, and 20 percent O_2/N_2. Several fresh bags were prepared and each blend was analyzed for response as ppm SO_2. Then each bag was doped with pure CO_2 to a level of about 10 percent. These bags were then run and the results of these tests are found in Table A-3.

It was apparent that by running the oxygen-nitrogen blends without any CO_2, certain effects could be observed. As the amount of oxygen in the sample decreased (and the nitrogen concentration increased), a positive response as ppm SO_2 was observed, even though no other compounds were known to be present. When the blends of about 12 percent CO_2 in various O_2/N_2 ratios were analyzed, it was found that the CO_2 and O_2 acted much the same in that the sum of the CO_2 and O_2 concentrations had the same quenching effect as the O_2 concentrations alone.

TABLE A-3. MULTICOMPONENT BLENDS OF $CO_2/O_2/N_2$ RESPONSE AS SO_2 IN MODEL 40 PULSED FLUORESCENT ANALYZER

Test	Concentration, %* CO_2	O_2	N_2	Response as ppm SO_2
1	-	0	100	10+
2	-	5	95	0.5
3	-	10	90	0.2
4	-	15	85	0.1
5	-	20	80	0.0
6	10 %	0	90	10+
7	10 %	4.5	85.5	0.5
8	10 %	9.0	80.0	0.2
9	10 %	13.5	76.5	0.1
10	10 %	18	72	0.0
11	100%	-	-	2.0

Initial conclusions regarding CO and CO_2 interferences indicate that these two exhaust species do not interfere as positive SO_2 response provided there is a sufficient quenching effect provided by oxygen in the sample. Problems could be present if direct exhaust samples are obtained and oxygen levels are low. Preliminary experiments indicate that oxygen levels above 5 percent have less than 0.5 ppm response as SO_2. In cases where a CVS air diluted sample is obtained, no interferences due to CO or CO_2 were observed.

NO_x Interferences

Five bottles of NO_x/N_2 were used to conduct initial NO_x interference experiments. These were also golden standards named by EPA Ann Arbor. Although these bottles were named as NO_x, they were actually NO in N_2 cylinders as verified by chemiluminescent analysis. The concentrations were selected to be typical ranges that might be expected in 1975 FTP testing. The results of this test are found in Table A-4. NO_x concentrations ranged from 42 to 220 ppm and the apparent interferences as ppm SO_2 varied from 17.0-36.0. This was the only gas tested which appeared to produce an increased response with increasing component concentration. It should be noted that N_2 zero gas produced some 10+ ppm response as SO_2.

TABLE A-4. MULTICOMPONENT BLENDS OF $NO_x/O_2/N_2$ RESPONSE AS SO_2 IN MODEL 40 PULSED FLUORESCENT ANALYZER

Test	Concentration			Response as ppm SO_2
	NO_x, ppm	O_2, %	N_2, %	
1	42	-	100	17.0
2	78	-	100	24.3
3	95.5	-	100	27.0
4	133.5	-	100	32.0
5	220	-	100	36.0
6	140	21	79	0.1
7	400	21	79	0
8	550	20	80	0.25
9	710	22	78	0.
10	1125	20	80	negative
11	1400	19	81	negative
12	1750	20	80	negative

There was a definite trend observed regarding NO_x concentration as a function of response as ppm SO_2, as shown in Figure A-1. Previous experiments involving CO and CO_2 interference checks indicated that the presence of nitrogen and the lack of oxygen could lead to apparent interferences. With this in mind, several blends of NO/N_2 were diluted with oxygen to obtain a nominal 20% O_2. The conversion of NO to NO_2 was immediately apparent due to the color change of the $NO \rightarrow NO_2$ reaction. Although the previous NO_x check involved NO/N_2 blends, this experiment actually was NO_2/Air and comparison is somewhat difficult. The concentration of NO_x ranged from 140-1400 in the bag samples analyzed. The O_2 and N_2 concentrations were relatively the same for purposes of this experiment. At any rate, the low concentrations (140-700) of NO_2/Air produced only slight response as ppm SO_2. At higher concentrations of NO_2, a negative response was observed for several gases.

It is difficult to make any absolute conclusions based on the data presented in Table A-4. Although NO/N_2 blends do give a positive response as ppm SO_2, it is impossible to determine the extent of NO/Air interferences due to the $NO \rightarrow NO_2$ oxidation in air. Bag samples obtained from a CVS are significantly air rich and have O_2 concentrations above 15 percent under most conditions. Since the CVS bag samples contain relatively low concentrations of NO_x diluted in air, it is not felt that any significant NO_x interferences will be experienced.

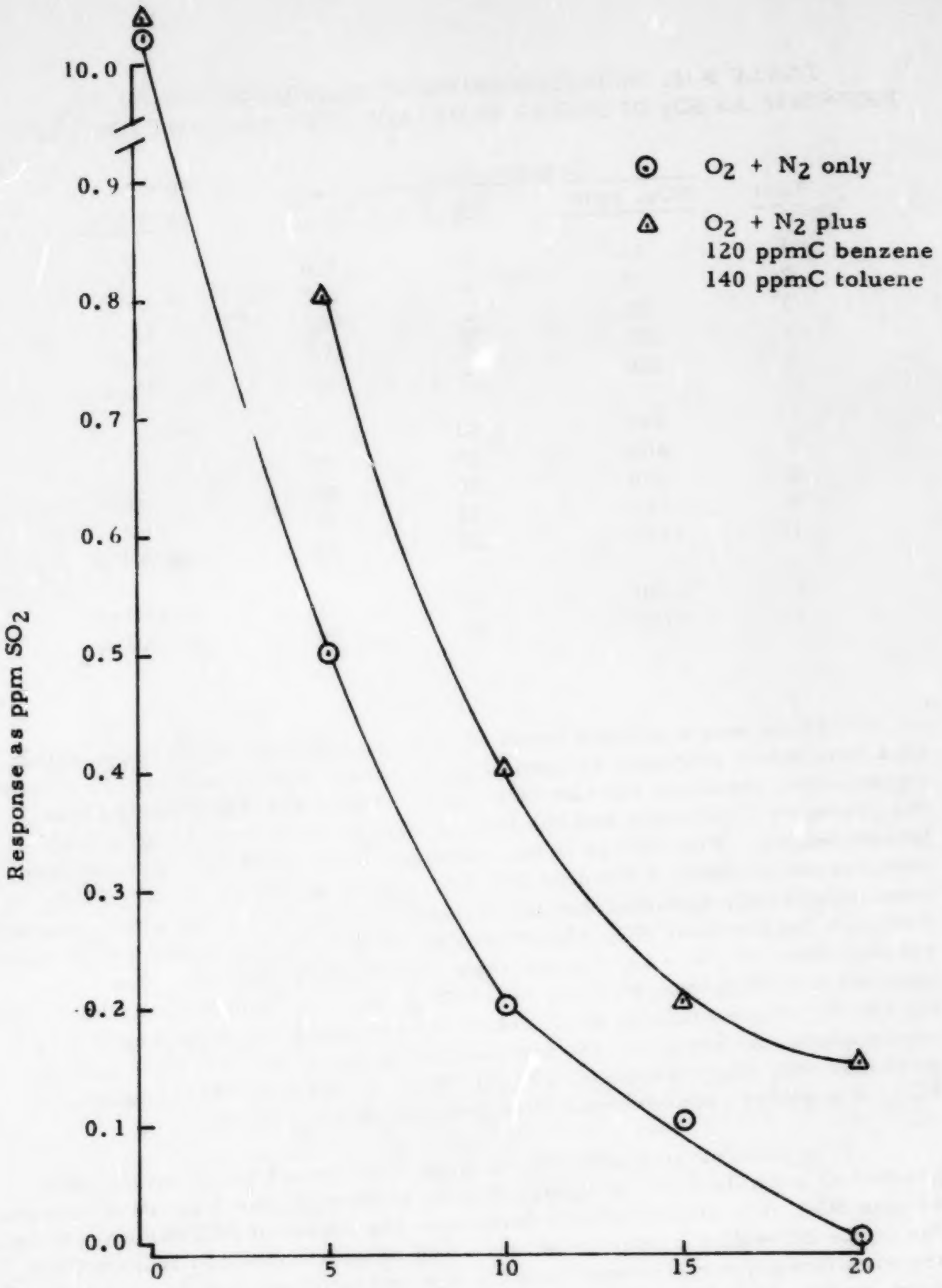


Figure A-1. The Effect of Benzene and Toluene in Various O_2/N_2 Blends as ppm SO_2 in Model 40 Pulsed Fluorescent Analyzer

HC Interferences to Model 40 Pulsed Fluorescent SO_2 Analyzer

Several experiments were conducted using typical hydrocarbon blends in N_2 and air. The initial tests were conducted using propane in N_2 and propane in air. The results of these tests are found in Table A-5. The golden standard span gases were originally thought to be air based gases, but during the tests it was found that the 34 ppm C bottle was actually a balance N_2 gas. This accounted for the fact that all of the other propane in air gases gave no response, whereas the 34 ppmC / N_2 gas gave an apparent response of 14 ppm SO_2. Hydrocarbon concentrations, varying from 25 to 1024 ppm C balance air, were found to produce no response as ppm SO_2.

TABLE A-5. PROPANE SPAN GAS RESPONSE AS SO_2 IN TECO MODEL 40 PULSED FLUORESCENT ANALYZER

Test	Concentration, ppmC	Balance Gas	Response as ppm SO_2
1	25	Air	0.0
2	34	N_2	14.0
3	168	Air	0.0
4	301	Air	0.0
5	1024	Air	0.0

It is suspected that the balance N_2 was responsible for the apparent interference in the 34 ppm C bottle. Once it was verified that typical air based HC span gases produced no interferences, it was decided to check the Model 40 pulsed fluorescent SO_2 instrument response to aromatic hydrocarbons. Two aromatic hydrocarbons typically found in automotive exhaust were selected for this experiment. These were benzene and toluene. The availability of several gases containing various ratios of O_2 and N_2 were selected for these tests. Baseline readings were obtained on each of these gases and these results are presented in Table A-6. A bag sample of each of these gases was obtained and a predetermined amount of benzene and toluene were added to each bag. Nominal benzene concentration was 120 ppm C and toluene concentration was about 140 ppm C.

The results of these experiments are illustrated in Figure A-2. In comparing the response as ppm SO_2 to the base O_2/N_2 blends to those same blends with added benzene and toluene it is apparent that some sort of interference due to aromatic compounds is present. It almost appears that the interference found in this test is an exponential function. Initial conclusions from this interference check indicate that samples containing less than 5 percent O_2 can have significant interference. These evaluations were conducted on the 0-10 ppm scale and the maximum interference that might be expected during CVS operation would be 0.2 ppm or 2 percent of full scale.

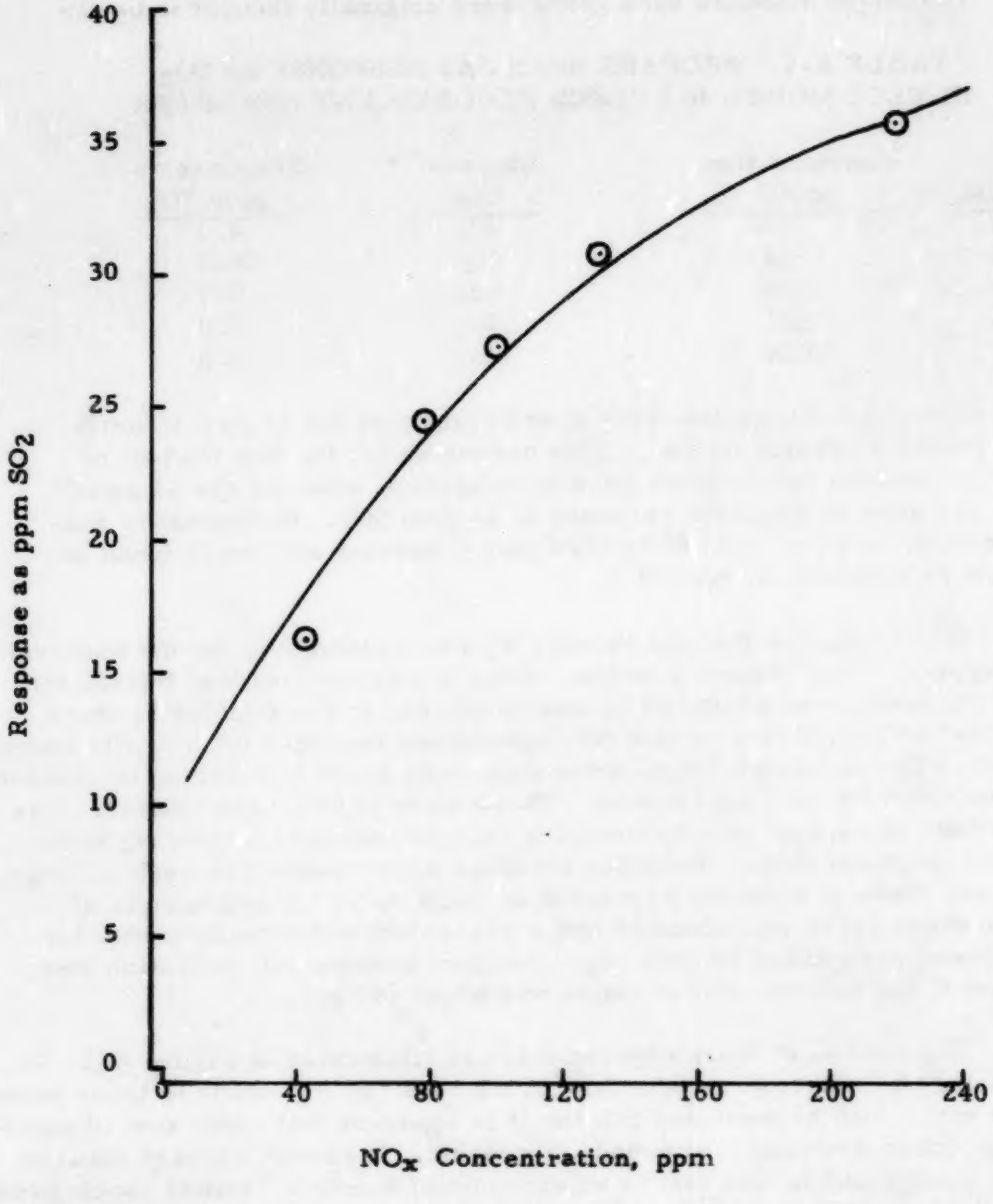


Figure A-2. The Effect of NO_x Concentration (balance N_2) on Response as ppm SO_2

TABLE A-6. MULTICOMPONENT BLENDS OF BENZENE, TOLUENE/O_2, N_2 RESPONSE AS SO_2 IN MODEL 40 PULSED FLUORESCENT ANALYZER

Test	Concentration, ppm C		Concentration, %		Response as
	Benzene	Toluene	O_2	N_2	ppm SO_2
1	-	-	0	100	10+
2	-	-	5	95	0.5
3	-	-	10	90	0.2
4	-	-	15	85	0.1
5	-	-	20	80	0.0
6	140	160	0	100	10+
7	140	160	5	95	0.8
8	140	160	10	90	0.4
9	140	160	15	85	0.2
10	140	160	20	80	0.15

General Comments of Model 40 Pulsed Fluorescent SO_2 Analyzer

Upon completion of the aforementioned experiments, several contacts were made with other individuals who had working experience with the instrument or was involved with Thermo Electron Corporation. The first contact was Glenn Reschke at General Motors. He had conducted numerous experiments with this model instrument, many of the same nature of the SwRI evaluations. Although his particular application was for use in direct automotive exhaust sampling, his conclusions regarding the various component interferences were essentially identical to those presented herein.

Further verification of individual component interferences conclusions was obtained from Dennis Helms of Teco. He re-iterated the items presented in this report and those indicated by Glenn Reschke. Recommendations for specific application to CVS type exhaust sampling have been previously incorporated into the exhaust sampling system.

It may be considered a concensus of opinion that sampling from any air-rich CVS system and using air balance SO_2 span gases and air zero gases minimize on potential interferences. Should direct exhaust sampling with relatively low oxygen concentrations (less than 5 percent), additional interference checks might be warranted.

Appendix B3.13

Status Report
ROAP 26 AAE
Task 008

Validate Engine Dynamometer Test Protocol for Control System Performance

Concept:

The initial concept underlying this objective was to test a control systems protocol being developed under contract at the Dow Chemical Company. These tests would confirm the ability of the test to measure the influence of fuel additives on various kinds of automobile emissions control devices including oxidation catalysts, EGR NO_x control devices and others. Resources available for the task (0.5 man-year and $15,000) were judged too small for complete development of a protocol.

In fact the Dow data arrived too late (July 1974) to have any impact on this portion of the in-house program, and experimentation was begun on the basis of very preliminary results from both Bureau of Mines and Dow. The Dow report has concluded that the candidate protocol was not satisfactory for assessing catalyst degradation, and this fact has had substantial impact on the in-house program in the last three months. Subsequent discussion will outline the problems associated with Control System degradation measurement, the candidate methods, and analysis of available contractor data on regulated emissions. Attachments include a report of the engine dynamometer hardware development problem including information on the subject of speed-load regulation, the analysis of contractor data, and a draft test protocol.

Protocol Development:

Early in the Dow contract a number of facts became apparent. First, individual components of an overall control system probably should not be tested individually. Catalysts, EGR packages, evaporative loss canisters, etc., are engineered to constitute an integrated pacakge system. Operation of the components is so interrelated that it is probably impossible to isolate the additive effect on EGR etc., separate from its overall effect on the system. Furthermore, there is essentially no information on the level of detrimental effect on such peripherals as PCV values, ECR, or evaporative canisters. Therefore, the required precision of testing required to isolate such effects cannot be assessed a priori'.

Such is not the case with catalysts. Catalyst degradation by lead, phosphorous, and sulfur compounds originating from fuel or lubricant additive packages has been much studied. The level of effects from known catalyst poisons and the mileage accumulation required to discover them is fairly well established. Thus, low levels of tetraethyl lead can cause significant decreses in catalyst activity in a few thousand miles.[1] Sulfur and phosphorous effects require 20-30 thousand miles before degradation becomes important.[2]

Since the influence of fuel additives on control peripherals is expected to be low and difficult to measure, any protocol to establish these minor effects must be either capable of high precision or rely on very extensive replication. Since these peripherals are part of an integrated system, the only rational choice is a test of the whole car with the variability that entails. Attempts to develop a high precision engine dynamometer test based on the present Urban Driving Cycle in the contract program were not successful in reducing the variability inherent in the basic system. Therefore, at present, it appears that only a very large automobile fleet test can detect these effects. At present the cost to perform such testing cannot be justified in terms of positive impact on ambient air quality for presently regulated emissions.

Therefore, concentrated effort was placed on determination of catalyst deterioration. The literature indicated that unregulated consumer driving can produce recognizable catalyst deterioration.[3] However, the variability in FTP testing makes detection of effects very difficult. Thus, on the basis of statistical analysis of Dow, Bureau of Mines and Calspan data, it was computed that the minimum number of car trials needed to reliably establish a 10% loss in catalyst activity is 86 in FTP testing.

Detection of a 25% loss in activity as a pass/fail criterion would require a minimum of 16 replications each of additive and control cars.

Mileage accumulation is also a serious problem. Catalyst deterioration occurs more rapidly at higher mileage values. On the basis of literature studies it appears that at least 25,000 miles is required to establish a 25% deterioration of catalyst activity for either CO or hydrocarbon.[2,3]

Description of the Protocol:

Catalyst activity can be determined most precisely by using a conventional engine operated at steady state, 30 mph level road load as a source of standard exhaust. Exhaust hydrocarbon level must be carefully controlled by continual monitoring of exhaust composition and carburetor adjustment. Thus, it is proposed to initially rate a series of catalysts on the dynamometer stand and instill these catalysts in test cars for mileage accumulation of 25,000 miles. At the end of the mileage accumulation phase the catalysts would be removed and re-rated on the dynamometer stand.

Catalyst performances rating parameters are % efficiency in hydrocarbon and CO removal, time from cold start to minimum hydrocarbon level, and rate of catalyst bed temperature rise. The test sequence suggested is similar to that used by auto manufacturers in screening studies and is generally referred to as the AC 813 test.

At present there is insufficient information from our in-house testing to establish the repeatibility of the test. If FTP testing is done in addition to the AC-813 test, the ability to detect a 25% increase in HC or CO can be controlled.

Conclusion:

A control system performance protocol is recommended which can control the chance of detecting a detrimental effect due to the additive at 25% using FTP testing. A second more sensitive test is proposed which is potentially capable of detecting much lower deterioration factors. Since this test is not as yet standardized, data from this source can only be used to indicate the possible pressures of small effects.

Appendix B3.14

FUEL ADDITIVE PROTOCOL DEVELOPMENT

Analysis of Bureau of Mines Data
Control Device and Gaseous Emissions Protocol Development Program

by Ronald L. Bradow, Chief, ETCS

I. Introduction

The gas emissions protocol development program at Bureau of Mines was designed to test the efficiency of a test schedule in assessing the influence of two fuel additives (Chevron F-310 and Ethyl AK-33-X) on emissions. A second function involved development of methods for detecting and determining any new toxic products resulting from the use of those additives. A report on this project from the bureau covers well the largely negative results of the search for new compounds. However, there is little discussion of the efficiency of the test schedule and procedures in assessing additive effects. This paper discusses the available gaseous emissions data on a statistical basis and points out the many shortcomings of the test program. Alternate approaches to the problem of assessment of additive effects are also discussed.

II. Test Schedules

The program seeks to evaluate fuel additive effects for non-catalyst cars. It was assumed that an engine dynamometer test stand could achieve higher reliability and repeatability in assessing additive effects than could be done with a fleet of cars. Therefore, the program required development of an engine dynamometer test procedure of high reliability. The procedure initially specified an elaborate break-in sequence involving a series of steady state operations designed to seat rings and wear in bearings, followed by a conditioning sequence of LA-4 routes to stabilize deposits. Engine dynamometer operation involved mileage accumulation by either repeated urban driving cycles or by the durability driving schedule with intermittant testing by the 1975 Federal test procedure. The cars were driven on the road in ordinary consumer driving with no specified cycle. At 1,000 mile intervals 1975 Federal test procedures were run on the cars.

The goal of increased test reproducibility with engine dynamometer tests was not achieved by any of the groups operating this procedure. In fact mismatch of vehicles both initially and during mileage accumulation was so poor as to make cross-car comparisons of little value. In the in-house experiments it has been found that careful raw exhaust measurement and attention to carburetor fuel flow adjustments at idle and at several steady state speeds is necessary to assure adequate vehicle and engine matching.

III. Analysis of Bureau of Mines Gaseous Emissions Data

Table I presents values from 1975 FTP emissions tests at the beginning of the test program, just before beginning additive injection, and the mean of all base fuel tests. It is immediately apparent that both stationary engines are lower in all emissions than the cars. The AK-33-X car appears somewhat higher in hydrocarbon and CO than the base car and this point will be developed statistically later. Both methane and ethylene emissions are also low in the stationary engines relative to the base car and the methane/ethylene ratio is also lower on that basis. Detailed consideration of the g.c. analysis data suggests a considerable effect of fuel composition on these results. Initial runs were performed with indolene fuel with a 35 vol.% aromatics content. Later the EPA reference fuel with a 24% aromatics content became available and a switch to that fuel was made. The switch was attended with a 35-40% decrease in methane, benzene and toluene in the base and F-310 car and a 15-20% decrease in these components in the apparently richer AK-33-X car. During mileage accumulation with the additives there was no apparent increase in any specific hydrocarbon emission. Variability in aldehyde data was high and no apparent differences were detectable on inspection.

Using the data in Table 1 and test variances for the control car, it is possible to decide statistically if the cars were originally matched. To test this point values of the Z statistic (distributed as t) were computed. Table II presents these values for comparisons of the test cars and engines with the control car. It is clear that the F-310 car and control car were matched, but the AK-33-X car has significantly higher CO and hydrocarbon emissions and must, therefore, be operating somewhat richer than the other two. The engine emissions were in every case lower than those of the cars and clearly, comparisons between engines and cars are invalid. It appears that the inertial loadings were too low for the engines and comparisons of peak horsepower or torque under some standard acceleration would be helpful in establishing this point.

The variance in basic emissions data on both engines and vehicles was similar to that previously reported by ECTD-MSPCP. Table III gives values of means, standard deviations and comparisons of means for all additive runs with test cars, and for AK-33-X runs with stationary engines. Again the car data is every where greater than that from the stationary engines. Standard deviations of the present tests are shown compared with those previously reported for fourteen similar cars by EPA-Ann Arbor. Generally variance of both car and engine tests are similar to the literature data.

Part B of Table III presents comparison of mean values for car tests using the t statistic. The most important conclusion to be derived from this data is that the AK-33-X car has significantly greater hydrocarbon emissions than either the F-310 or base cars at the test end. Of course this was also true at the beginning of the test cycle. If the initial and final values for that car are compared, it was found that there is no significant difference in hydrocarbon but the carbon monoxide is significantly lower at the end of the AK-33-X test. Thus, it is impossible to assign any clear effect to either additive on the basis of these car tests. Since only two individual engine tests were conducted to high mileage, it cannot be definitely established that, during mileage accumulation, by sheer chance both engines changed mechanically to produce the observed test result. Therefore, even though the difference between the base fuel and additive fuel tests have statistical significance, the significance cannot ascribed uniquely to the additive. Clearly, either sufficient control data must be obtained to assure that the changes observed cannot be ascribed to mechanical changes or sufficient mileage experiments must be run to allow removal of vehicle or engine influences.

It is important to note that none of the Bureau of Mines, EPA or Dow engine dynamometer testing has found any improvement in repeatability over vehicle testing. Comparison of the variances of test data can be made in this case using the F statistic and Table IV presents the data. In no case where any of the Bureau of Mines tests significantly different in variability than literature 1975 FTP vehicle tests.

Table V presents a comparison of all stationary engine data indicating the similarity of F-310 and base fuel data on both engines.

Table VI presents comparison data from Calspan, Dow and EPA-RTP. As in the Bureau of Mines tests, the individual automobiles have a wide variety of emissions characteristics. The Calspan cars are significantly mismatched as were the initial tests with the EPA cars. Since these EPA tests were run, a considerable effort has been expended in maintaining the repeatability of the vehicles. This has involved periodic determination of raw exhaust composition and, hence, fuel air ratio at idle, 15, 30, 45, and 60MPH steady state conditions.

Since the influence of fuel additives on emissions may be indirect; for instance, the additive may increase or decrease fuel-air ratio, the additive effect is indistinguishable from mechanical changes. A test with few vehicles may be very difficult to control with the most careful maintenance. Considering the test variability, it is possible to calculate the minimum number of tests required to discover a real difference of any given percentage in hydrocarbon NO_x emissions. To find a 10% increase because of the additive, a minimum of 86 tests is required for both the additive and control cars. For a 5% increase 344 tests are required.

Conclusion

The variability in all gas analysis data in the fuel additive contract program strongly suggests that an engine dynamometer FTP protocol cannot adequately assess the minor influences which fuel additives are likely to exert. Only gross effects (in the order of 30% or greater) in the emissions values can be detected by the certification test procedure in a reasonable number of replications, say 10 or fewer.

In order to successfully test the additive effect, the test itself must be greatly simplified possibly to the point of simply determining steady state fuel-air ratios. The only alternative would seem to be a large fleet test of 100 cars or more.

TABLE I

Analysis of Bureau of Mines Initial Emissions Data

Final Report EPA-IAG-097(CD)

	grams/mile				
				Sta. Engine	
Vehicle/Fuel	Base	F-310	AK-33X	A	B
Hydrocarbons					
Initial	2.92	2.76	3.09	2.18	1.37
Begin additive	2.78*	2.77	2.92	1.29#	1.79°
Mean Value [a]	2.72	2.72	3.14	1.38	1.59
N	5	5	6	6	4
CO					
Initial	46.7	59.5	74.4	22.0	18.2
Begin additive	63.6*	62.1	63.5	17.5	20.5
Mean value [a]	56.9	64.5	71.6	20.8	17.8
N	5	5	6	7	4
NOx (corr.)					
Initial	4.62	4.55	4.85	3.42	1.79
Begin additive	5.60*	5.81	5.16	2.86	2.86
Mean value [a]	5.23	5.16	5.49	3.21	2.46
N	5	5	6	7	4
Methane, ppmc					
Initial	16.86	17.39	17.49	7.23	7.11
Begin additive	15.04	12.81	14.61	7.85	9.70
Ethylene, ppmc					
Initial	17.79	19.95	19.75	11.46	---
Begin additive	17.02	18.81	23.32	10.99 (6,400 mi.)	9.70
Aldehyde					
Initial	---	---	---	---	---
Begin additive	0.103*	0.086	0.088	0.074	0.109

* 4550 miles
# 4950 miles
° 3990 miles
a mean of all preadditive runs

TABLE II

Comparison of Initial Car and Engine
Emissions Data
Basis - Control Car

Statistic	σ	Z*			
		F-310	AK-33-X	A	B
HC	0.32	0	2.18	7.22	5.27
CO	9.9	1.20	2.47	6.29	5.89
NO_x	0.71	0.154	0.610	4.83	5.82
$\sqrt{1/N_1 + 1/N_2}$		0.64	0.60	0.58	0.67
D.F. #		8	9	9	7
Value of Z for significance, 95% confidence level		1.86	1.83	1.83	1.89

$$* \quad \frac{\bar{x}_1 - \bar{x}_2}{\sigma\sqrt{1/N_1 + 1/N_2}}$$

# D.F. = $N_1 + N_2 = 2$

TABLE III

A. Variance of Bureau of Mines Data-additive Runs

Car or Engine		grams/mile Base	F-310	AK-33X	A^3	B^3
HC						
	$\bar{x}$	2.48	2.65	3.48	2.10	2.27
Bumines	σ	0.32	0.20	0.42	0.44	0.44
EPA [1,2]	σ	0.32	0.34	0.45	0.27	0.29
CO						
	$\bar{x}$	65.3	53.8	62.0	19.0	29.0
Bumines	σ	9.9	11.4	8.0	2.8	5.7
EPA [1,2]	σ	11.9	9.8	11.3	3.4	5.3
NOx(com)						
	$\bar{x}$	5.40	5.35	5.47	3.35	2.98
Bumines	σ	0.71	0.67	0.29	0.47	0.34
EPA [1,2]	σ	0.49	0.49	0.50	0.30	0.27

B. Comparison of Means - Values of the t statistic; N=10

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\frac{\sigma_1^2}{N_1} + \frac{\sigma_2^2}{N_2}}}$$; 95% confidence interval t= 1.81

	Base XF-310	Base AK-33X	F-310-AK-33X	AK-33X -initial AK-3
HC	1.42	6.80	5.00	1.58
CO	2.40	0.82	1.86	1.98
NO_x	0.10	0.29	0.35	0.09

1. "Test Variability", Memo Karl Hellman to John DeKaney, Jan. 1973.
2. Computed on the basis of 13.0% σHC, 18.2% σCO, and 9.09% σNO_x for GM cars on 1975 FTP as per ref. 1.
3. AK-33-X runs

TABLE IV

Comparison of Variance - BuMines and EPA Data

a.) Additive Runs

EPA data from Ref. 1 - N_1 = 28, N_2 = 10
F5% - 2.75

	Values of the F Statistic				
	Base	F-310	AK-33-X	Eng.A*	Eng.B *
HC	1.0	1.71	1.07	1.68	2.34
CO	1.20	1.16	1.41	1.73	1.22
NO_x	1.45	1.37	1.72	1.01	1.34

* F-310 runs - corrected for level differences by assuming constant relative σ

TABLE V

Stationary Engine Data

Additive Fuels

Engine	Base		F-310		AK-33-X	
	A	B	A	B	A	B
HC						
$\bar{x}$	1.63	1.78	1.56	1.69	2.10	2.27
σ	0.29	0.24	0.12	0.093	0.44	0.44
CO						
$\bar{x}$	22.1	26.9	25.7	38.8	19.0	29.0
σ	3.4	9.0	3.4	9.8	2.8	5.7
NO_x						
$\bar{x}$	2.96	3.05	2.62	4.08	3.35	2.98
σ	0.38	0.71	0.34	0.16	0.47	0.34

TABLE VI

1972 Chevrolet Engine and Vehicle Emissions Data

Base Fuel

A. Calspan Data - 3 cars

		A	B	C	DOW Engine Dyno
HC	$\bar{X}$	1.31	1.47	2.10	0.99
	σ	0.20	0.13	0.31	0.50
	N	8	8	7	7
CO	$\bar{X}$	24.49	30.81	39.78	22.08
	σ	4.90	3.55	4.80	4.70
NO_x	$\bar{X}$	3.39	3.08	3.05	---
	σ	0.42	0.40	0.51	---

E. EPA-ORD data - 3 cars - 1 stationary engine

		308	309	310	Stat. Eng. Y
HC	$\bar{X}$	1.62	1.18	1.50	1.39
	σ	0.19	0.17	0.30	0.17
	N	10	10	7	7
CO	$\bar{X}$	51.0	50.8	30.3	20.2
	σ	6.4	8.5	3.6	3.8
NO_x	$\bar{X}$	3.37	3.46	3.20	1.93
	σ	0.70	0.44	0.34	0.51

Appendix B3.15

PROPOSED EPA PROTOCOL
CONTROL SYSTEM PERFORMANCE

1. Scope.

The Administrator, United States Environmental Protection Agency, if he determines that a fuel additive offered in commerce has a significant probability of causing deterioration of control system performance, may require of the manufacturer of such an additive to perform the tests contained within this protocol. Under the provisions of the protocol, a fleet of 16 matched pairs of catalyst-equipped cars shall be chosen and emissions tested by the Federal Certification procedures. The characteristics of the fleet shall be submitted to the EPA who will determine if the vehicle fleet chosen conforms to a fair selection of catalyst-equipped cars in service and whether or not the cars are fairly matched. On receipt of approval of the test fleet from EPA, the additive manufacturers shall remove catalysts from the cars and perform an initial converter- efficiency test, using a V-8 engine mounted on a chassis dynamometer. On completion of the initial tests, the catalytic converters will be reinstalled on the automobiles and mileage accumulated. Oneof each automobile pair shall be operated exclusively on a gasoline containing the additive at the maximum concentration to be registered. The other member of the pair shall be operated on the same base gasoline without the additive. The cars shall be placed in ordinary consumer driving service without control of maintenance or pattern for 25,000 miles, except that the total time shall not exceed 2 years. At the end of that period, the cars shall be tuned up to manufacturers' specifications, and Federal certification emissions tests shall be run. The catalytic converters shall then be removed from the cars and tested by the chassis dynamometer procedure once more. Data from certification and dynamometer testing shall be submitted to EPA for determination of detrimental effect of the additive.

The provisions and dimensions of the test protocol were selected by statistical considerations. On the basis of knowledge of the variability inherent in Federal Certification Testing, it is possible to control the probability of finding false positive and false negative responses to the protocol. It has been determined that the probability of errors of both the first and second kind shall be controlled to 5% if the catalyst deterioration response is as great as 25%. The minimum number of pairs of vehicles required for a statistically valid experiment on this basis is 16.

2. Submission of Car Fleets.

The manufacturer shall select new passenger cars in pairs to comprise the additive test fleet. The cars shall be selected to be fairly representatitve of the current year's production catalyst-equipped cars and shall include V-8, in-line-6, and 4 cylinder engines in a variety of vehicle weights. Cars may be immediately tested; however, the proposed vehicle fleet selection must be submitted to EPA for approval. The approved car fleet must be then tested by the Federal Certification Test Procedure for light-duty vehicles (Federal Register, Nov. 12, 1972 as ammended by Federal Register, Jan. 14, 1974) with the following exceptions: Since the vehicles will have been already certified, no Part I submission of characterisitics need be made; the evaporative emissions tests, heat-build-test, and preliminary vehicle preparation shall be omitted, except that a preparative Federal Urban Driving Cycle shall be driven on the day immediately before the certification test. A series of three consecutive certification tests shall be performed with each vehicle. The data from these initial tests shall be submitted to EPA for determination of the comparability of additive and control cars. On receipt of approval of comparability, the additive manufacturer shall then remove the catalytic converters from each car and perform a second engine dynamometer test for converter efficiency as described below.

3. Converter Efficiency Test

A V-8 engine of approximately 350 cubic inches displacement manufactured by an American-based automobile manufacturer as a production engine in the model years 1972 or more recently shall be used as an exhaust generator and shall be mounted on an engine dynamometer test stand. The dynamometer may be of the hydraulic, eddy-current, or electric motor-generator types. The dynamometer shall be capable of absorbing, measuring, and controlling the engine load to ± 1.0 ft-lb. of torque at simulated 30 mph level road load for that engine, mounted in a vehicle of 4000 lb. intertia weight equivalent. The level road load chosen shall not be less than 15.0 nor more than 20.0 ft-lbs of torque. The engine shall be tuned and operated so as to produce, after 15 minutes of warm-up operation, an exhaust gas corresponding to the following specifications:

CO - 0.4 to 0.6 Vol. %
Hydrocarbons(FID) - 500 to 750 ppm C vol./vol.
O_2 - 2 to 3 vol. %
Temperature - 730 ± 30° F

Catalytic converters shall be mounted in the exhaust system of this engine in a manner consistent with their use in a vehicle.

Thus, catalysts designed to treat the whole exhaust of a 300 cu.in. or greater engine shall be mounted so as to treat the whole test engine exhaust. Catalysts meant for 4 or 6 cylinder engines or for one bank of a V-8 shall be mounted in the exhaust of one bank of four cylinders of the test engine. A by-pass section of exhaust pipe, controlled by means of coupled diverter valves at either end, shall be constructed around the converter such that the engine may be warmed up initially and its exhaust then diverted through the initially cool converter. Tests of hydrocarbon and CO content of the pre-catalyst exhaust shall be made by drawing a sample of exhaust from the exhaust pipe section immediately preceding and immediately following the converter. Samples of gas may be obtained by use of a metal bellows pump, an ice-bath water knock-out trap, stainless steel transfer lines and fittings. Samples of dried exhaust gas shall be pumped directly to approved CO, CO_2, and hydrocarbon analysis instruments. Analysis for CO and CO_2 shall be conducted using non-dispersive infrared analyzers and analysis for hydrocarbons by flame ionization analyzers; all such CO, CO_2, and hydrocarbon analyzers shall conform to the specifications set forth in the Federal Register standards for light-duty vehicle certification (Federal Register, Nov. 12, 1972).

The gas transfer system shall be capable of a flow rate sufficiently great that a sample of raw exhaust shall have a residence time in the combined transfer and analytical system of no greater than 1 second. The overall analytical system shall be capable of a 90% response to a 10 ppm pulse in hydrocarbon concentration in the raw exhaust in 3 seconds. Records of test results shall be made for each test using strip chart recorders or other data-logging devices capable of information up-date every 10 seconds or faster.

4. Dynamometer Test Procedure.

The engine shall be started and operated on the test fuel at the test condition for 15 minutes or more to assure stabilization of exhaust conditions. To begin the converter performance test, diverter valves are switched, allowing exhaust to enter the converter. The initial time, catalyst temperature, and exhaust analysis before and after the converter are recorded. Engine conditions are maintained at 30 mph, level road load, for 600 seconds during which time exhaust composition and catalyst temperatures are recorded. At the conclusion of the test the engine may be shut down and the catalyst may be cooled by drawing room air through the converter. Successive experiments shall not be run before the catalyst temperature drops below 130° F.

The results of 6 such tests for each converter shall be submitted to EPA in the form of data tables of computed percentage break-through of hydrocarbons and CO and certified copies of strip chart or data-logger records indicating time to minimum values.

5. Fuels.

Two types of fuels shall be used in the additive tests, certification and mileage accumulation fuels. All gasoline used in engine and vehicle testing shall conform to the specifications given in the Federal Register, Nov. 12, 1972, except that the Reid vapor pressure shall be between 9 and 10.5 psi. The mileage accumulation fuel shall conform to SAE recommended practices for distillation and Reid vapor pressure characteristics in the climate areas in which the vehicle tests are operated.

Other specifications for mileage accumulation fuels are given below:

Table 1
Fuel Properties

Aromatics	20 min.	30 max.
Olefins	5 min.	15 max.
Saturates	balance	
Lead	less than 0.01 grams/gallon	
Phosphorous	less than 0.003 grams/gallon	
Sulfur	less than 200 ppm wt./wt.	

6. Conclusion.

The above test sequence is derived from similar tests conducted in the automotive industry, specifically the AC-823 test. Modifications have been made to test converters more nearly in the conditions typical of their use in cars built to the interim 1975 standards.